RAPHAEL MELDOLA

CHEMISTRY

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CONTENTS

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INTRODUCTORY

THE history of civilization reveals the fact
that all highly developed nations in the course
of their evolution have passed through phases
characterised by the culmination of various
human activities, physical and intellectual.
Not that it is implied by this statement that
the manifestation of extreme activity of a
particular kind at one period was accompanied
by a decline, or was developed at the expense
of all other forms of activity.   The lesson of
history is that, concurrently with the general
national activity, certain ages have witnessed
special activities or have attained particular
maxima of development which have served
to stamp the age with some general charac-
teristic.   Thus, there was an age of Philosophy
in ancient Greece, of Militarism in ancient
Rome, of Sacred Art in mediæval Italy, and
of Dramatic Poetry in England during the
Elizabethan period.   The influence of such
epochs has extended perceptibly or imper-

ceptibly from a remote past down to the present time ; the recognition of this influence is embodied in the familiar adage that we are the heirs of all the ages. The special activity of the present time, Science, is one that we believe is destined to influence the future more profoundly than any of those activities which reached their culminating points in former ages.

In stating that we are now living in an age of Science, it is meant that we are getting into closer communion with Nature than has hitherto been possible. From the time when man became an observing and thinking being, he must have been impressed by natural phenomena ; but at no former period, so far as history has preserved records, has there been such intense activity in the questioning of Nature—in the systematized observation of facts, and in the endeavour to arrive at a knowledge of causes. It may be said that, among the more advanced nations, mankind is gradually beginning to grasp that great truth which in former ages was realized only by a few specially gifted individuals—the truth that the human race, although the intellectual crown and summit of terrestrial life, is not detached from and independent of its surroundings. The anthropocentric notions

which dominated thought in early times are slowly being replaced by that broader view which makes man a part of Nature—an organism adapted to his environment just like any other organism, but having the supreme advantage of practically unlimited adaptability by virtue of his intellectual development. It is now beginning to be perceived that this power of adaptation is synonymous with a knowledge of Nature's methods—in other words, that the present well-being and the future progress of the human race is dependent upon the development of Natural Science.

The recognition of the principle that man's dominion is inseparably bound up with scientific progress is embodied in Tennyson's lines :—" The crowning race ; Of those that eye to eye shall look on knowledge ; Under whose command is Earth and Earth's ; And in their hand is Nature like an open book."

This recognition has been brought about in modern times by the labours of those who have devoted and are devoting their lives to the study of Nature at first hand. It is the active army of original investigators who, in the first place, have become cognizant of the supreme importance of their work to the present and future welfare of the race. The

realization of the truth that Nature is to the earnest student " an open book " has become the trumpet call of the present age. The worker in the domain of Science is prompted by the knowledge that his results, directly or indirectly, immediately or prospectively, may be utilized for the benefit of humanity. His achievements, although strictly humanitarian in their ultimate bearing, cannot, however, be weighed and measured by a narrowly practical standard. The level of natural knowledge which has now been reached, and which is annually being raised, is the result of patient and laborious research, often extending over many years, sometimes over a lifetime. But only a small proportion of the work accomplished is of immediate utility ; and that which is obviously useful to man is but the final stage of a long series of antecedent gropings after truth. The popular appreciation of Science, to be of real value to the nation, should, therefore, be independent of the spirit of narrow utilitarianism, for no investigator who enters upon a definite line of work can foresee when or how his results may become of practical value, or whether they will ever lead to any practical applications. If the progress of the nation is dependent—as we are now beginning to

realize—upon its general appreciation of Science, that appreciation must be of the highest and broadest character—it is Science in the abstract, and not purely utilitarian concrete knowledge, which must be raised to the level of one of the most exalted branches of human culture.

The modern awakening of the spirit of scientific inquiry has resulted in an activity which is in itself responsible in some measure for the slow progress towards the attainment of that high standard of popular scientific culture which we desire to see established. The active workers are a numerous and ever growing body, and the boundaries of knowledge are being extended with such rapidity in every direction that the educated layman who can follow with intelligence the various developments of Literature or of Art finds himself unable to cope with the progress of Science. Nor is this surprising when we find that even the workers themselves, having necessarily to specialize in order to achieve results of value, are unable to keep pace with the progress of discovery in domains outside their own field of research. Moreover, the constant discovery of new facts and principles, and the concurrent revision or extension of scientific doctrine is apt to discourage the would-be

learner who, without any special scientific training, has had his mind deprived of plasticity by an inelastic education in subjects for which the materials are gathered entirely from books and not directly from Nature's records.

Another obstacle in the way of the general diffusion of scientific culture is the technical language which every branch of science has found it necessary to invent in order to give precision to the description of new facts, and for the formulation of new principles. But, while admitting that the technicalities of modern scientific language from the popular point of view interpose difficulties, it must be borne in mind that for the actual workers they are labour-saving contrivances. Although the terminology may appear formidable to the uninstructed, it must not be forgotten that every term and every symbol corresponds with some natural reality, or with what according to existing knowledge is believed to be a reality. The reality is generally capable of being expressed in simpler terms than would appear from its symbolical expression; the underlying idea is generally less complex than the language which has been found necessary to define it with scientific precision.

But, apart from all such difficulties, in view

of the daily increasing importance of Science as a prime factor of national development, the educated layman can no longer afford to ignore the achievements of that great international army which is waging perpetual warfare against ignorance of Nature's methods. In this quest for knowledge, there is no distinction of race, or creed, or country—all workers are co-operating for the general cause ; a truth wrested from Nature becomes the common property of mankind. Such truths cannot be lightly set aside, or crushed out of existence by the older learning ; they are revelations to man as distinct, as eternal, and as far reaching in their consequences as any proclaimed by the seers and prophets of former ages.

Granting, therefore, that the reader wishes to be put in possession of the existing state of scientific knowledge, it must at the outset be realized that Science never pauses on her onward march ; there is no " existing state " of knowledge in the sense of finality. She has no dogmatic creed to proclaim ; she is aware of her fallibility ; and her strength lies in her knowledge that it is Nature which is infallible, and man but an interpreter with limited power of observation and reasoning. The ground covered by Science is, moreover,

so vast that it must also be recognized that, for the practical purposes of study and research, sub-division into departments is absolutely necessary. Not that these sub-divisions are representative of any natural reality; they are expressive rather of the imperfect state of our knowledge. In view of the limitations of human faculty, it is both necessary and expedient that the worker should confine himself to some particular department; but, in accepting this principle as a matter of convenience, the student must not commit himself to the belief that this sub-division indicates a want of unity in Nature. On the contrary, the most advanced thinkers have come to believe in the unity of Nature and to recognize that the ideal towards which research is tending is the unification of knowledge into one general Science or system of Philosophy. There may be work for countless generations before this ideal is reached, but even now there are indications in every direction that natural knowledge cannot be confined in water-tight compartments; the barriers, confessedly artificial, are being broken down, and the inter-relations between the various sciences are becoming both more numerous and more intimate with the progress of discovery. The tendency towards coales-

cence is shown by the creation in modern times of such subjects as thermodynamics, astrophysics, chemical physics and physical chemistry, electrochemistry, thermochemistry, biochemistry, and biophysics.

CHAPTER I

THE SCOPE OF CHEMISTRY—THE NATURE OF
CHEMICAL CHANGE—CHEMISTRY AN EX-
PERIMENTAL SCIENCE

The Scope of Chemistry.—The Science of
Chemistry, as is, no doubt, already known to
the reader in a general way, is essentially a
materialistic science in so far as it deals with
matter.   It belongs to a division known as the
physical sciences, a designation applied in
order to distinguish such subjects from those
which, like Zoology, Botany, Physiology, etc.,
deal with life, and which are, therefore,
grouped as the biological sciences. This
classification is convenient as representing
the existing state of knowledge ; whether
such sub-division corresponds with some
underlying fundamental reality is a debate-
able question concerning which no dogmatic
pronouncement can at present be made.
But as with all attempts at rigid classification,
so here it will be found that no absolute
barrier can be erected between the two

16

groups. Living matter, whether lowly or highly organized, is as subject to physical and chemical conditions as non-living matter. The Physics and Chemistry of the living organism are no longer regarded as impenetrable mysteries beyond the scope of legitimate scientific investigation. Modern Chemistry does not recognize that rigid definition which in former times restricted its scope to " dead matter " ; in that borderland between the two main groups of sciences, there is now at work a new school of investigators who are attacking the mysteries of vital chemistry in the same spirit as that which has prompted research into every other department of science. It is realized that the living organism has solved chemical problems which we have as yet been unable to approach by our known methods—but this is regarded as an incentive, and no longer as a deterrent, to further inquiry. On the other side, the biologist deals with living organisms not only from the point of view of classification, distribution, bionomics, evolution, etc., but he also concerns himself with their physical and chemical activities, with the inner mechanism of the life processes. Physiology, in the broad sense, has now become the meeting-ground of the physical and biological sciences.

B

In placing Chemistry in the front rank as a science concerned with matter, we thereby associate it with other sciences which also deal with matter, and especially with Physics, its nearest and natural ally. In view of what has been said concerning the conventionality of our schemes of classification, it is perhaps unnecessary to insist upon the impossibility of drawing a sharp line of demarcation between Chemistry and Physics. No other branches of science furnish such numerous and such striking examples of interpenetration. Physical methods of studying the properties of matter are used by chemists, and chemical methods are being adopted by physicists. All that can be said definitely is that those general properties of matter, such as gravity, which are independent of the specific nature or composition of the substance, belong more exclusively to the domain of the physicist. But even in this case, the chemist is dependent upon gravitational effect for the determination of weight—the most important of known methods for dealing with matter quantitatively.

Whenever we pass from the general to the special, and consider in detail the changes in matter brought about by the action of physical forces, it will be seen that the nature

or amount of change is generally influenced by the inherent properties of the substance, or, in other words, by those specific characters which are as truly chemical as physical. Thus, heating and cooling cause bodies to expand or contract, a change which, in general terms, may be said to be physical. But in this case it cannot be said that the change is independent of the inherent nature of the substance; for, when the expansion or contraction is measured quantitatively, it is found to be a specific character, and therefore of chemical significance. Again, a ray of light is bent or refracted in passing from one medium to another of different density; here, also, the general effect is said to be physical. But the actual amount of bending, as measured quantitatively, is found to be determined by the specific character or composition of the medium; and the relationship is so close that in certain classes of cases the measurement of this quantity gives information to the chemist concerning the nature of the substance. One of the most striking illustrations of the association of Physics with Chemistry is furnished by the results obtained by the study of the action of electricity upon matter in the gaseous state, a field of research which has led in

recent times to suggestions of fundamental importance concerning the constitution of matter. It is evident that such questions are of equal significance to Physics and to Chemistry; but the modern developments in this direction are as yet hardly mature enough to incorporate with the established body of chemical doctrine. As an earlier illustration, however, nothing is more instructive than the history of the development of spectroscopy. A gas or vapour when raised to a sufficiently high temperature to glow or become self luminous emits light which appears to have colour. In purely physical terms, this is explained by the statement that the colour is the result of the impression produced upon the eye by ether waves of particular lengths or oscillation frequencies. But, here again, when we go into details, and analyse the light emitted by such glowing gases, we find that the particular kind of radiation is a specific character of the radiating matter—sufficiently specific for diagnostic purposes, so that particular kinds of matter can be identified, whether here, or in the sun, or in the most distant stars and nebulæ. The chemist and physicist and astronomer here join hands; the science based upon this property of

matter is both astro-chemical and astro-physical.

It is obvious from such considerations that Chemistry is all-embracing in its scope ; its branches ramify in every direction, and its roots underlie the most diverse departments of science. Since it concerns itself with matter wherever it exists and can be brought within the ken of its methods, it may be regarded as the common meeting-ground of all the natural sciences. From the purely utilitarian point of view, no other science can be said to be more intimately bound up with the immediate welfare of man. The prime needs of civilized nations—the raising of crops for food-stuffs, the utilization of fuel for the generation of power or for warmth, the manufacture of useful products from raw materials, the production of the multifarious necessary materials required in every-day life, all depend at one stage or another upon a knowledge of the principles of chemical science and their practical application.

The Nature of Chemical Change.—Chemistry does not restrict itself to the study of matter simply as it exists, either naturally or artificially ; it is, above all, the science which concerns itself with the changes or transformations of matter brought about by the

agency of physical forces, or by the action of one form of matter upon another. In so far as the mere consideration of change in matter is concerned, Chemistry and Physics overlap to a very large extent. For practical purposes it is, however, convenient in the present state of knowledge to distinguish between physical and chemical change. If, under the influence of physical agencies such as heat, light, electricity, etc., matter undergoes some change which is not permanent, it is considered to be a physical change. If these or other agencies bring about a permanent change or transformation of one kind of matter into a totally different substance, the action is claimed as coming within the province of Chemistry. Following up the illustration previously given concerning the action of heat, a bar of iron is longer when it is hot than when it is cold ; but the change, *i.e.*, the increase in length, is not permanent, because the bar regains its original length on cooling. This is an example of physical change, and, even if the expansion were permanent, it would not be regarded as a chemical change, because there is no transformation of material—the bar is the same substance, iron, both hot and cold. If the iron is heated to a very high temperature, it

undergoes further changes, first becoming soft, and then, as the temperature rises, becoming liquid, so that it can be poured out of the containing vessel. These, again, are physical changes of state, because the material is still iron ; by the process of fusion its form may be permanently changed, but its substance is unaltered.

Although such properties of matter are described as " physical," they become of chemical significance when we pass from the general to the special—when their study is made comparative. Thus the expansion of iron at a given temperature as compared with the expansion of other substances at the same temperature, or the temperature at which iron melts, *i.e.*, passes from the solid to the liquid state, may be claimed as physico-chemical properties, because they are specific and not general ; other forms of matter may or may not have the same degree of expansibility and the same point of fusion. When, however, intensely heated iron is freely exposed to the air, or is plunged into water, it undergoes a change in appearance ; the surface becomes covered with an incrustation or scale of something which is no longer iron. In this case, the change is permanent so long as the new substance remains under ordinary

conditions ; iron is there, but in a disguised form, and can only be recovered from the new substance by violent treatment, such as heating to an extremely high temperature in contact with coal or carbonaceous matter. The iron in this case has undergone a chemical change ; it has become transformed into a different substance. Even without the application of heat, iron on exposure to air and moisture, as every one knows, becomes " rusty," i.e., converted into a reddish substance which, like the " scale " just described, contains iron, but is no longer that material ; in rusting, iron loses all its original physical and physico-chemical properties. It is changed in hardness, tenacity, specific gravity, electric conductivity, fusing point, magnetic character, colour, and so forth. It is with transformations of this kind that Chemistry is especially concerned.

Examples illustrative of chemical change might, of course, be multiplied indefinitely ; the case selected on account of its familiarity, viz., the transformation of iron into other substances, will, however, serve to put the reader into the position of an inquirer wishing to know what happens to iron under the circumstances specified. Now, the first impression produced when such cases are

thought over seriously is one of marvel at the thoroughness of the change. The more extensive one's experience—the larger the number and variety of the transformations studied—the more wonderful does the phenomenon appear, even to those whose daily occupation has familiarized them with such manifestations of the properties of matter. Then follows naturally the question whether chemical change really is, as it may appear to be at first sight, the actual transmutation of one form of matter into another—is iron scale or iron rust simply transmuted iron ?

This last question may appear a very simple one ; but it took more than a century's work to answer it, and it was not until the answer was given in general terms that Chemistry began to emerge from the empirical and to pass into the scientific stage. It is impossible within the compass of the present work to attempt the historical treatment of the subject : suffice it to say that the answer to the above question is in the negative. Iron rust or iron scale is not simply transmuted iron, but iron in combination with something else. That something else is supplied by the air or water ; and the proof of this is furnished by the fact that the iron gains in weight when it is changed into rust or scale. The nature

of the other component need not concern us just now ; it is the general principle which is of prime importance : that which at first sight might appear to be a case of transmutation turns out to be a case of transformation due to the combination of the iron with another form of matter. Two further questions thus suggest themselves :—Is transmutation in the strict sense of the term known or conceivable ? Is all chemical change the result of the combination between different kinds of matter ? In answer to the first question, it may be said that the theoretical development of modern Physics in connection with the constitution of matter has made the notion of transmutation conceivable, but the decision from this point of view must be left to the physicists. Whether cases of transmutation are actually known is a chemical question which is now under consideration.

The answer to the second question is of more immediate importance for the adequate conception of the nature of chemical change. It has already been stated that the change in the case of iron under the conditions described is the result of combination—of the addition to the iron of some other substance. This other component of iron rust and iron scale is supplied by the air or water with which

the iron is brought into contact, as is proved by the fact that iron may be heated or exposed for any length of time in a closed vessel from which air and water are absent without being transformed into scale or rust. It may at once be stated that this other component is a form of matter known to chemists as oxygen, a substance which under ordinary conditions is a colourless gas, but which condenses to a liquid at an extremely low temperature. The transformation wrought by chemical change appears in a more striking light when it is considered that from solid iron and gaseous oxygen there arises a black, brittle scale, or a reddish, earthy rust, both solid, differing from each other, and absolutely unlike their generators. Moreover, underlying the fact that two different forms of matter can when combined give rise to two distinct substances is another great chemical truth, the bearing of which will be considered subsequently. The would-be inquirer will also want to know in what form the oxygen exists in air and water respectively, since it has been described as a gas, and, although air is a gas, water is a liquid until its temperature is raised sufficiently to convert it into vapour or steam. So that the suspicion arises that the oxygen may not be in the same condition in air as it

is in water; and another point is thus raised for future consideration. And if the reader is prompted by that spirit of active inquiry which is the prime instigator of all scientific progress, he will demand a more direct proof of the statement that iron rust and iron scale contain oxygen, because the mere gain in weight proves nothing more than that the iron has taken up something else. But the proof of this assertion necessitates a broader grasp of facts, and must be postponed until the general outlook has been widened. In the meantime, the main point—whether all chemical change is the result of combination between different kinds of matter—must be dealt with.

In order to prepare the way for further developments, it may at once be stated that the answer to this last question is in the negative. The reverse process, *i.e.*, the undoing of the combination between different kinds of matter, may also lead to transformations which are as distinctly chemical as those resulting from combination. And when we come to inquire more deeply into the process of combination, even in the most familiar and apparently straightforward cases, such as the rusting of iron, it is found that the conditions are in reality very complex—

so complex that the most delicate methods have recently had to be employed by expert experimenters in order to determine the nature of the transformation, and whether that which at first sight appears to be a simple case of direct combination between iron and oxygen may not be a case of indirect combination. In fact, the formation of new substances by direct combination as known to chemists is generally an artificial process, *i.e.*, the result of experimental conditions imposed by the experimenter. Indeed, the very forms of matter which have been referred to for the purposes of illustration are, humanly speaking, artificial products, since iron, although found to a limited extent, as such, in nature, is for all practical purposes obtained by chemical processes from its naturally occurring compounds ; and the fact that the substance of iron scale is found in large quantities as a natural mineral, magnetite, suggests interesting lines of inquiry respecting the past conditions of the earth, under which the iron and oxygen were enabled to combine so as to produce in some cases magnetite, and in other cases the substance of iron rust, which is also found as the mineral hæmatite, or, in combination with water (hydrated), as limonite. Was magnetite formed by the

direct combination of iron with oxygen, by the action of water upon hot iron, or by some other process ? Was hæmatite formed from iron by some process analogous to that of rusting ? These questions are not raised for the purpose of answering them, because in the present state of knowledge no decisive answer can be given, but in order to illustrate still further the all-embracing scope of chemistry. From the simple observation that iron forms certain compounds with oxygen, there arise questions which bring Chemistry into the domain of Geology. There is, in fact, a science of Geo-chemistry yet awaiting development.

Although chemical change by direct combination is now a rare phenomenon in nature, it may have been and, no doubt, was the predominant mode of material transformation during that period of the earth's history when our globe was cooling down from an igneous condition. But high temperature chemistry at the present time is, excepting under volcanic conditions, an artificial chemistry, *i.e.*, brought about by human artifice; and the study of chemical change in all its phases enables us to state that direct combination is but one out of many possible modes of bringing about such transformations of matter. The further consideration of these various

modes may for the present be deferred; but it must at once be realized that there are in operation in nature processes of chemical change other than by direct combination, which are everywhere going on, subtly, silently, and generally imperceptibly—light, air, and water on the surface of the earth, and heat and pressure below are slowly effecting such transformations of matter; every living organism is an active centre of chemical change. In other words, the consideration of the nature of chemical change must not be allowed to lead to the belief that the process is purely artificial. There is a natural chemistry both of non-living and of living matter of which our knowledge is still very imperfect, and towards the better understanding of which our laboratory studies are gradually leading us.

Chemistry an Experimental Science.—A very erroneous impression would be gained if it were imagined that the data of chemical science can be obtained by direct observation as in the case of Astronomy, or of the biological sciences, in which large bodies of ready-made facts are offered for investigation. Natural chemistry, as already indicated, is both complicated and recondite. The mineral components of our globe represent the products

of chemical changes which may have taken ages for their completion; the chemical processes which go on in the living organism are still shrouded in mystery. We can produce artificially in our laboratories large numbers of these products of Nature's laboratory, mineral, animal, and vegetable; but, great as are the achievements of modern Chemistry in this direction, it must not be concluded that we have thereby disclosed Nature's methods. We cannot compete with Nature in her scale of working—either in time, in mass of material, in temperature, or in pressure. We do not, therefore, go to Nature in the first place for ready-made facts in our endeavour to penetrate the inner secrets of those properties of matter upon which depend its capabilities of undergoing chemical change; but we impose our own conditions—in other words, we cross-examine Nature by experiment. By experiment, we mean trial— the observation of facts obtained under conditions which are under control, and which can, therefore, be varied in known ways. The principle involved in this method is that which is responsible for the development of all those branches of science which are not dependent upon the direct observation of uncontrollable phenomena. By studying

simple cases under controllable conditions, and observing the effects of changed conditions, we endeavour to connect phenomena such as chemical change with their antecedent phenomena, *i.e.*, to connect effect with cause ; and so, from the simpler and known relationships established by the experimental method, we pass to the more complex and unknown relationships which exist under natural conditions.

In this way there has been acquired such knowledge of the inherent properties of matter as could never have been acquired by the direct observation of ready-made facts. Chemistry—the most typical of the experimental sciences—has so far penetrated the inner mysteries of matter as to have called into existence an infinitude of new compounds, *i.e.*, of forms of matter absolutely unknown in nature. In claiming the achievements of synthetical chemistry as triumphs of modern science, it must, of course, be understood that no claim is made to our having mastered Nature in the sense of conquering matter. Our chemistry is not an unnatural chemistry ; all that has been achieved has been made possible only by our having learnt those potentialities of matter which, in their ultimate essence, may for ever elude our methods of

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investigation.   Every artificial substance pro-
duced in our laboratories or factories is but
the materialization of potentialities already
inherent, and which, so far as we know, may
have been present in matter from the begin-
ning of the existing order of things :—" Yet
Nature is made better by no mean, but Nature
makes that mean : so, o'er that art, which,
you say, adds to Nature, is an art that Nature
makes."

It must be clearly understood, therefore,
that Chemistry as a science cannot be learnt,
in the strict sense of the word, by merely
reading about it.   The would-be student may
be informed of the existing state of knowledge
through books of a descriptive or historical
character ; but he must realize that all the
information given—all the general principles,
all the laws and generalizations that we are
enabled to enunciate, have been based on facts
gleaned by laboratory work.   That is why the
foundations of modern Chemistry are said to
be well and truly laid.   The apparently simple
observation from which we set out—the
rusting of iron—is in reality an experiment,
because the transformation is under control.
For instance, we can modify the state of
aggregation of the iron by reducing it to fine
particles by a file, or, if brittle, we can grind

it to a fine powder (iron swarf); and if some of this finely divided iron is exposed for some days in a confined volume of air, such as is contained in a bottle inverted over water, we can find out that the air as a whole is not absorbed, but only a certain proportion of it, about one-fifth of its volume. So that the oxygen which combines with the iron is picked out by the latter by a selective process, and anything that is not oxygen is left uncombined, and the rusting ceases as soon as all the oxygen is used up. An experiment of this kind teaches us, therefore, that chemical change is preferential, inasmuch as the iron combines with only one form of matter present in the air, and, under the conditions of the experiment, refuses to combine with any other substance contained in the bottle. From this it further follows that air contains something besides oxygen; and the question as to the condition in which oxygen is present in the air, which was previously raised (p. 28) is thus answered to the extent that it is permissible to state that it is in a form easily removed by iron at ordinary temperatures. The bearing of this will be seen subsequently.

It must be noted, also, that it has been throughout assumed as a condition of rusting that the air must be moist, *i.e.*, that it con-

tains the vapour of water. That statement is based upon experiment, because if we remove all the water vapour from the air by absorbent substances, of which many are known to chemists, then no rusting takes place, although there may be oxygen present. So that oxygen and water vapour are both essential for the production of the chemical change in this case. Moreover, there is also present in air a small quantity of another gaseous substance, which is known as carbon dioxide —the gas which is familiar to all as giving rise to the evolution of bubbles, *i.e.*, the effervescence when a bottle of mineral water or " sparkling " wine is opened. This gas is present only to the extent of three or four volumes in ten thousand volumes of air, so that refined and delicate methods of measuring its quantity have to be adopted. It is believed by some experimenters that the co-operation of this gas with oxygen and water vapour is also essential for the rusting of iron, while others have come to the conclusion that the iron itself can exist in either a sensitive or insensitive state with respect to its power of combining with oxygen, and that carbon dioxide is not essential. All these facts are mentioned in further illustration of the importance of the experimental method, and

to enforce the lesson already inculcated, that the apparent simplicity of a familiar chemical change disappears when Nature is rigidly cross-examined under controllable conditions with the object of finding out how and why such transformation takes place in any particular case.

It must not be imagined that the resources of experiment are exhausted when, as in the foregoing illustration, the chemical transformation of iron has been traced to its faculty of combining with oxygen.   In addition to the facts, a principle has been revealed —the principle that iron, regarded as a form of matter, has its likes and dislikes, since it selects the oxygen from the air, and leaves four-fifths of some uncombined gas behind. That gas, it may at once be parenthetically noted for future reference, consists mainly of another form of matter known as nitrogen. As a deduction from the facts already observed, the question next arises whether iron shows preference for other substances. Thus we might proceed to test this question experimentally by mixing iron with other familiar substances, such as sand, or sugar, or charcoal, or chalk, or sulphur.   To make the question more searching we should naturally in such a case give the iron every chance, by

using the finely-divided substance in the form
of filings or dust, and we should grind this up
with the other materials. Under these cir-
cumstances, we should find that nothing more
than mixtures would be obtained—the pro-
ducts would not come within the conception
of chemical change, because the iron is still
present as such, and could be separated from
the sand or sugar, etc., by means of a magnet ;
or the sugar could be dissolved out by water,
leaving the iron behind ; and so with the
other mixtures, separation could be effected
by appropriate methods.

But if iron is ground up with that metallic
looking solid known as iodine—a substance
obtained from the ashes of sea-weeds, and
familiar in pharmacy—we find that, if a suffi-
cient quantity of iodine is used, a grey product
is obtained from which iron cannot be readily
separated ; the iron and the iodine have lost
their individuality through chemical change.
Thus, under the conditions in which iron
refuses to combine with sugar or charcoal
or the other substances, it combines with
iodine, and the principle of preferential action
is thus extended. This is what in old time
chemistry would be expressed by saying that
the iron had an " affinity " for oxygen and
iodine, but not for nitrogen, or sand, or chalk,

or any of the other substances. And now, prosecuting the inquiry still further, we should find that the application of heat may bring about combination in the case of the sulphur-iron mixture, but in no other of the mixtures referred to, although we should discover incidentally that the sugar was totally transformed on heating, with the production of charcoal, that the sand and charcoal were unchanged, and that the chalk, although apparently unaltered in appearance, had, if strongly heated, become transformed into another substance, lime. When heated, the mixture of iron and sulphur suddenly begins to glow—developing heat by the combination of the materials—and the product, when cold, consists of a dark coloured, brittle solid from which, provided sufficient sulphur has been added, iron cannot be readily separated. Here again, chemical change has taken place.

It will be obvious from these illustrations that Chemistry is an art as well as a science; the carrying out even of simple experiments necessitates manual dexterity, skill, judgment, and a knowledge of the various contrivances or forms of apparatus available for particular purposes. And so we are brought back to the fundamental proposition that our scientific

knowledge has been built on a foundation furnished by the art of the experimentalist. We can learn from books what are the general scientific conclusions at any particular period ; but no amount of reading will make a learner into a proficient chemist.

CHAPTER II

CHEMICAL COMBINATION AND MECHANICAL MIXTURE—AIR A MIXTURE AND NOT A COMPOUND—PHYSICAL SEPARATION OF THE COMPONENTS OF AIR

Chemical Combination and Mechanical Mixture.—The consideration of those profound modifications in matter which result from chemical change will have made it evident that a clear distinction must be made between the products of chemical combination and mechanical mixtures. This point is very generally misunderstood by the uninstructed, and is often a stumbling-block to the student on his first introduction to chemical science. The difficulty arises from the circumstance that the product arising from a combination of two different substances does not, as common sense might lead us to suppose, partake of the characters of both components, but is a totally distinct form of matter. The common sense notion applies to mechanical mixtures, for these do partake of the characters

of their components—their properties are intermediate between those of the substances mixed, and can be made to vary indefinitely by varying the proportions of the ingredients. But these ingredients, whatever they may be, are always present as such in the mixture. However finely we may grind up a mixture of, let us say, iron dust and chalk, we can always pick out the iron by a magnet, because it is a property of iron to be attracted by a magnet, while chalk is not thus attracted. Moreover, a mechanical mixture is never homogeneous : such mixtures may be made apparently homogeneous by grinding to a very fine powder, but, if we examine some of this powder under a microscope, the different particles of the components can easily be distinguished. The product of chemical combination, on the other hand, is always homogeneous—its particles, however finely divided by mechanical means, are all alike in appearance and properties. The mixture of iron dust and sulphur referred to in the last chapter is visibly a mixture when sufficiently magnified ; but if, after heating, the product of combination is ground up to a powder, no magnification will reveal either iron or sulphur *provided the materials were present in the right proportions.*

This last condition introduces a new set of considerations—the quantitative relations between the combining materials. Herein we shall find a characteristic of chemical combination of such fundamental importance that this part of the subject must be fully dealt with at a later stage, when the general nature of chemical change has been more thoroughly grasped. In the meantime, it will be instructive to give one or two illustrations of the popular misconception of chemical transformation. We often see it stated, for example, that metals are extracted from their ores, or that dyes, perfumes, explosives, etc., are extracted from coal-tar. To the uninitiated, these statements might convey the impression that the metal, say iron, is present as such in the ore, or that the dyes, etc., are contained in the tar, and that the process of extraction is nothing more than a sort of mechanical separation of the metal or the dyes from the other materials with which they are mixed. Nothing could be further from the truth than this conception of the process. There is no free iron in iron ore ; there are no ready formed dyes or perfumes in tar. The liberation of iron from the oxygen with which it is chemically combined in, let us say, hæmatite is the result of

chemical transformation which the ore is made to undergo by heating it with some other substance, such as the carbonaceous fuel referred to in the last chapter, which enters into chemical combination with the oxygen. That is why iron was previously declared to be a product of artificial chemistry —in this case we call it a metallurgical process, because iron belongs to a class of substances known as metals. So, also, are the dye-stuffs, etc., artificial products ; they are obtained from certain substances contained in and separated from the tar, but the generating substances—the raw materials— are not themselves dye-stuffs. The latter arise from their non-tinctorial generators by a series of operations which involve chemical transformation at every stage. This last case is among the most striking illustrations of the marvellous transformations brought about by chemical change. Even when a naturally occurring ore does contain a metallic substance which, like gold, has to be separated from the other materials with which it is mixed, the extraction is very seldom a purely mechanical process : chemical extraction is generally resorted to.

Although the fundamental distinction between chemical combination and mechanical

mixture has, no doubt, been made clear by
the illustrations given, it is not always easy
to decide off-hand whether any given substance
is a mixture or a true chemical compound.
Let it, in the first place, be realized that since
Chemistry has for its scope the study of the
transformations of matter in all its forms,
the particular state of physical aggregation of
the matter concerned in any case of chemical
change is of minor importance from the
chemical point of view. From every day
experience the reader has been made familiar
with the existence of matter in the three
forms known respectively as solid, liquid,
and vapour, or gas. The interconvertibility
of these forms is generally dealt with from the
physical side in works on Physics, although,
as has already been pointed out, the specific
properties of different forms of matter with
respect to the conditions which determine
their state of aggregation are also of chemical
significance. Illustrations of chemical change
resulting from combination between different
kinds of matter in different states of aggrega-
tion have already been given. Thus, solid iron
combines with gaseous oxygen and with solid
iodine giving rise to chemical compounds.
The selection of the oxygen from the air by
iron when it rusts has been referred to as a

fact indicating that the oxygen is present in the air in an easily removable form. But this fact does not in itself decide the question whether the oxygen in the air is chemically combined with the nitrogen or the other substances which are known to be present in air. It does not answer the question—Is air a chemical compound, or a mechanical mixture? We know of many true chemical compounds which are gaseous at ordinary temperatures, and we know also that iron and other substances can decompose some of these compounds, *i.e.*, can undo the chemical combination by taking out one of the components and leaving the other. This will be made clearer as we proceed; but the bare statement of these facts will suffice at present to enforce the lesson that the scientific interpretation of experimental evidence requires both caution and judgment.

Air a Mixture, and not a Compound.—It is, of course, well known that air is not a chemical compound, but a mixture of oxygen and nitrogen with small quantities of other gaseous substances, such as carbon dioxide, water vapour, and traces of a few other gases, which will be spoken of in a later chapter. If, therefore, the observation that rusting iron withdraws the oxygen is not decisive, how,

then, it may be asked, has this conclusion
been arrived at ? So far as mere homo-
geneity is concerned, the air answers to the
definition of a chemical compound : it has
the same properties from whatever part of
the world it comes.   The rusting iron experi-
ment gives within quite narrow limits the
same quantitative result with air from any
quarter of the globe, if the volume of oxygen
withdrawn is measured.   The conclusion that
air is a mixture is based upon convergent lines
of evidence, the consideration of every one
of which will introduce us to new general
principles.   Two or three of these lines may
be advantageously followed up now.

In the first place, let us ask whether there
is any criterion of chemical combination
beyond that general change in character of the
transformed substance which has so far been
considered.   To put the case in another way
—is there any method of ascertaining, apart
from the appearance and properties of the re-
sulting product, whether two substances when
mixed together enter into chemical combina-
tion, or remain simply in admixture?   There
is one such indication of chemical combination
which, when observed, is a very sure sign
that something more than mechanical mixture
has taken place, and that is the development

of heat. This is a point of fundamental significance, and will require further elaboration. It is not always possible to detect the heat of chemical combination, because in many cases the transformation takes place very slowly, and the heat is dissipated too rapidly to enable us to measure it. The combination of iron with oxygen is a case in point. There is no doubt that heat is developed when iron rusts, but that is a case of slow chemical combination. Now, although the state of physical aggregation of the matter entering into combination is, as already stated, of minor importance so far as concerns the nature of the final product, yet it is obvious that the state of physical aggregation may influence the rate of combination. In the case of a solid combining with another solid, or with a liquid or a gas, it is evident that the more intimately the combining materials are brought into contact the more rapid will be the chemical combination. That is why, in such experiments with iron as have been described, it was thought desirable to use the metal in a finely divided form. It is simply a case of presenting as large a surface as possible to the other substance. But, however finely we may divide iron by mechanical processes, it is not possible to increase the rate

of its combination with oxygen to a sufficient extent to enable us to detect the rise of temperature on rusting.   All that can be said is that iron sheet would rust more rapidly than a solid block, and that iron filings or iron dust would rust more rapidly than either block or sheet iron.   It is possible—although not easy practically—to prove this experimentally by measuring the rate of absorption of oxygen from air by iron in different states of division.   It is possible, also, by a chemical process to obtain iron in such an extremely fine state of division that it possesses what are known as " pyrophoric " properties, becoming red hot on being shaken into the air from the tube which contains it.   In this case, the combination between the microscopic particles of iron and the atmospheric oxygen takes place so rapidly that the evolution of heat produces a visible effect.

The development of heat as a criterion of chemical combination is thus likely to be most observed in cases where the combining materials are brought into the most intimate contact.   No state of physical aggregation can insure more intimate contact than the gaseous state, for this is the most mobile condition of matter, and gases mix freely with each other in all proportions.   Now, the

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main constituents of the air, oxygen and nitrogen, are gases ; they can be obtained in various ways by chemical processes, and they can be mixed together in the same proportions as those in which they exist in the air, viz., four volumes of nitrogen and one of oxygen. The resulting product is a gas having all the properties of air ; no change of temperature takes place, and the characters of the mixture are intermediate between those of its components. That is one reason why air is regarded as a mixture, and not as a compound.

The homogeneity of product in this case, therefore, is in a sense accidental—it is the result of the extreme mobility of the gaseous form of matter. It may be asked, now, if the homogeneity of air—which is supposed to be characteristic of a true chemical compound—is thus a violation of that criterion of chemical union which has been previously set up. Is the homogeneity real, or is it only apparent ? This question may, in the first place, be answered hypothetically. Supposing, by some magnification of the power of vision, it were possible to see the actual particles of which a gas is made up, different gaseous forms of matter might be expected to present different appearances. The particles might be quite dissimilar to an

imaginary being with such an exalted sense of vision—they might differ in size or shape or weight, or they might be moving about with different velocities. Thus, our hypothetical being might be supposed to know an oxygen particle from a nitrogen particle; and if a sample of air were submitted to him for examination, what would he find ?   He would see the oxygen particles and the nitrogen particles mixed up, moving about among each other, and bombarding the sides of the containing vessel, colliding and rebounding— all in a higgledy-piggledy way; but the two kinds of particles would throughout their evolutions remain distinct, each after its kind; there would be no fusion together or combination, and each kind, even if temporarily deformed by collisions, would preserve its weight as well as its average rate of movement.

This ideal picture of the inner state of affairs in gaseous matter is a physical conception, and is in harmony with all those general properties of gases which the student learns from the science of Physics.   If the picture be a true representation of the facts, it follows that the homogeneity of air is apparent, and not real; its particles, could we see them, would not be all alike as they would be if it were a

true compound. The only approach towards homogeneity that could be realized by such a mixture would be the possession by equal volumes taken at random of absolutely the same number of particles of the two gases. It is for the sake of simplifying the argument that attention has been concentrated upon these two components, because the oxygen and nitrogen together make up the main bulk of the air. But what has been said with respect to these two gases is true for the other minor components, such as water vapour and carbon dioxide, and all the other gases which exist in mere traces. Our imaginary being with supernatural power of vision would be likewise capable of distinguishing between and following the migrations of the fewer particles of water vapour and carbon dioxide in the course of their wanderings among the greater crowd of oxygen and the still greater crowd of nitrogen particles. With these other components, there is no combination in the chemical sense.

So much for the hypothetical answer to the question whether air is really homogeneous. Of course, the ideal supernatural vision is unattainable by any human contrivance, so that direct proof of heterogeneity is not to be looked for by any such means. But if

heterogeneity can be proved experimentally, then it will be admitted that there is justification for the hypothetical answer.   There are many such proofs—that which is unrealizable visually, viz., the discrimination between the different kinds of particles, can be realized by other means; and it is of the utmost importance to note that the means about to be indicated are non-chemical.   The importance of this reservation will become apparent when it is restated that any attempt to separate the components by the action of some other form of matter which exerts a selective action—as in the case of rusting iron—is always open to the suspicion that there may have been chemical decomposition.   As already pointed out, the removal of the oxygen or nitrogen or of any other constituent gas by chemically combining it with some other substance leaves the question of the original condition of the oxygen, etc., in the air an open one.

A simple observation will serve to show that one of the components, viz., the water vapour, is not chemically combined.   It is, no doubt, a familiar fact with those who wear spectacles or eye-glasses that, on coming from the cold outer air suddenly into a warm room, the glasses become dimmed by a deposit

of moisture—a deposition of dew upon the glass. The same thing is observed if we take a glass of iced water into a warm room ; the *outside* of the glass becomes covered with moisture. That means that our supernatural being was right when he observed particles of water vapour moving about among the oxygen and nitrogen particles. The interpretation of the observation is that the water vapour is only retained in the air because the air is warm ; warm air contains more water than cold air, so that, when warm air is cooled by contact with cold glass, it deposits some of its water vapour on the glass in the form of droplets of liquid water or dew. The separation of water as such from the air by the mere lowering of temperature indicates that the water was there, although in an invisible or vaporous state : had the water been chemically combined with any other constituent of the air it could not possibly have been liberated by the simple process of cooling.

The proof that the nitrogen and oxygen in air are not chemically combined involves the application of methods which are probably unfamiliar to the general reader. Their very unfamiliarity makes them instructive, because their consideration will bring us into contact with other fundamental properties of matter.

Let it be borne in mind that, in this particular case, we are dealing with matter in the gaseous form. The particles of matter in this state possess, as we have already explained, perfect freedom of movement; and our imaginary being has been supposed to see the different kinds of particles moving about with different velocities. Now, the average speed of these particles is a property which is dependent upon the nature of the gaseous substance; it is, in fact, a physico-chemical property, and is connected with the relative weights of the particles. We shall have to consider later how these weights are ascertained; but it is easy even at this stage to form a mental picture of light and heavy particles all mixed up together, the lighter particles moving more rapidly than the heavier particles. If, therefore, the oxygen and nitrogen particles are independent entities, and not chemically combined, and if the two kinds of particles have different weights, and are within a given volume of air moving with different velocities, then a process of mechanical sorting seems conceivable.

The foregoing conception can be verified experimentally, because it happens that the nitrogen particles are a little lighter than the oxygen particles—in fact, a nitrogen particle

has seven-eighths the weight of a comparable oxygen particle. If we could pass air through a sieve with very small meshes—small enough to bear comparison with the actual size of the particles, and not large enough to allow the whole mixture of particles to pass *en masse* through the interstices—then more of the light than of the heavy particles would get through in a given time, because the lighter particles are moving the more rapidly. The air which passed through such a sieve ought, consequently, to be richer in nitrogen, and the air which was left behind ought to be richer in oxygen. Now, the fine-meshed sieve which enables this conception to be verified may be any substance with extremely minute pores, such as unglazed porcelain, or plaster of Paris. Of course, the reader is familiar with the physical fact that air cannot be confined in a porous vessel if it is under pressure, or if there is no air outside the vessel to balance the pressure of the air within. If, therefore, air be drawn through a glass tube containing a plug or diaphragm of some fine-pored material, the proportions of the gases will be altered—we should draw out of the tube an air containing more nitrogen than the normal proportion, and there would be left behind an air containing more than one-fifth of its volume

of oxygen.   Such a purely mechanical separation as this is another proof that the nitrogen and oxygen in air are not chemically combined.

It will be noted that, throughout this discussion of the question whether air is a mixture or a compound, it has been assumed that the gaseous substances, oxygen, nitrogen, etc., consist of " particles."   This conception of the constitution of gases has been referred to as a physical conception, and the further development of the idea in its physical aspects must be pursued in works on Physics. We are here brought face to face with one of the most striking examples of the interdependence of two branches of science. So far as the conception has been made use of in this chapter, the main object has been to introduce the reader to the current view that the substances, nitrogen, oxygen, etc., although gaseous under ordinary conditions, are not to be looked upon as continuous, but as discontinuous in structure.   The supposed magnification up to the stage of visibility has been imagined to reveal a discrete or granular constitution—the gases have been supposed to consist of extremely minute particles. This is the modern view of the constitution of matter in all states of aggregation.

It is, historically speaking, a very ancient

conception, but it has been put upon a scientific basis in modern times by the joint labours of chemists and physicists. All forms of matter, solid, liquid and gaseous, if we could but see into their inner constitution, would be found to consist of particles, these having perfect freedom of movement in gases, more restrained powers of movement in liquids, and comparatively little freedom of movement in solids. It will be seen subsequently that these minute components of matter which have hitherto been defined by the intentionally vague term " particle " must, from the chemical point of view, be defined with much greater precision. The broad physical conception of matter as composed of discrete particles has been translated into more concrete terms by modern Chemistry with such marvellous success that we may be said to have made some progress towards the realization of those supernatural powers of vision which have been ascribed to our imaginary being.

Physical Separation of the Components of Air.—The transition from the solid to the liquid, or from the liquid to the gaseous form of matter, or the reverse series of changes, are physical phenomena made most familiar to us in the case of water, which we all know in

the forms of ice, water, and steam, or water vapour. The precise temperatures at which these changes of state take place are physico-chemical characters of the various substances, and are dependent upon the heat imparted to or withdrawn from the substance, the heat so imparted or withdrawn being generally measured on the scale of a thermometer. Thus, the point at which a change of state takes place is said to be the melting-point or point of fusion of the substance if it passes from the solid to the liquid state, or the freezing-point or point of solidification if the change is from the liquid to the solid state. The temperature at which a liquid overcomes the atmospheric pressure and passes suddenly into the state of vapour is known as the boiling-point. The measurement of temperature, the determination of melting-points and boiling-points, the various thermometers and their scales, the effects of pressure, etc., are all dealt with in books on Physics and on practical Chemistry. It will suffice for the present to state that in Chemistry the Centigrade scale is always used, and on this scale the zero-point (0°) is the freezing-point of water, and the boiling-point of water under the average atmospheric pressure of 76 centimetres is marked 100°.

Thus the description of the various states of physical aggregation of matter is made more definite when we are enabled to associate with each substance its specific physico-chemical characters of melting-point or boiling-point. We say, for example, that above 100° water exists as vapour, and at 0° as ice. And what is true for water is true for other liquids and for other gases; for it is now known that those forms of matter which, like nitrogen or oxygen, are gaseous at ordinary temperatures are really the vapours of liquids whose boiling-points are so low that they are never reached under any natural terrestrial conditions. In other words, we should have to cool air down to a temperature of more than 190° below the freezing-point of water in order that its physical state might be changed and the gaseous mixture condensed to a liquid. Now, the liquefaction of air and of other gaseous forms of matter has been effected on the large scale in recent times—a feat that must be regarded as among the great achievements of modern science. The principle made use of is essentially physical, and cannot be considered in detail here. All that need be said is that it is a self-cooling process, for, when a highly compressed gas is allowed to escape suddenly from its containing vessel,

it cools itself by expansion, and the cooled air can then be made to cool another lot of escaping gas, and so on by a summing-up of coldness in a continuously cooling cycle until the point of liquefaction is reached. Air is thus obtained as a limpid liquid not unlike water in appearance.

Starting, then, with air reduced to a liquid in some suitable apparatus by the method described, it is obvious that, when such a liquid is allowed to rise in temperature by exposure to the atmospheric temperature, which in this country averages about 200° above the boiling-point of liquid air, the latter will begin to boil, and so resume again the gaseous state. But if the oxygen and nitrogen of the air are not chemically combined, then liquid air must consist, not of a definite compound, but of a mixture of liquids; and if the various constituents have different boiling-points, then, as the liquid air passes into gas, it might be expected that the constituent which passed most readily into gas, *i.e.*, which had the lowest boiling-point, would boil off more rapidly than the constituents which had the higher boiling-point.

To make this point quite clear, the reverse process may be considered, viz., the cooling down of a mixture of gases to the point of

liquefaction. In this case, the most easily condensible gas would be that which had the highest boiling-point, so that the liquid obtained from such a mixture would be richer in that component. Now, the boiling-points of the main constituents of the air, oxygen and nitrogen, are about 183° and 196° below the freezing-point of water respectively ; in other words, nitrogen boils about 13° lower than oxygen. Consequently, on the assumption that air is a mixture and not a compound, the mere physical act of liquefaction might be expected to upset the composition, since the oxygen with the higher boiling-point would condense more readily than the nitrogen with the lower boiling-point. This is actually found to be the case—the gaseous air recovered from liquid air contains nearly double the quantity of oxygen contained in normal air. Moreover, if liquid air is allowed to boil by exposure to the ordinary temperature, the nitrogen boils off more rapidly than the oxygen, and there is finally left a liquid residue which, on being allowed to gasify, is found to be still richer in oxygen, so that a continuous process of separation is effected without calling in the agency of any other form of matter capable of removing the oxygen or the nitrogen by

chemical combination.   It is a case of
separation by purely physical means—a
separation which would have been impos-
sible if the oxygen and nitrogen had
been chemically combined. Thus there is
furnished another proof that the air is a
mixture, and not a chemical compound.

CHAPTER III

Chemical Change in its Quantitative Aspect.— Air has been selected as a type of a mechanical mixture because of its familiarity as the medium in which we live. All the chemical processes which go on in the world of life, animal and vegetable, and which are manifestations of " vitality," are dependent upon one or another of the constituents of that gaseous envelope which enwraps our globe. Thus, animals require oxygen and plants carbon dioxide, and both forms of life require nitrogen, which is supplied directly or indirectly from the atmosphere. We speak now of the gaseous components of the air as forms of matter with the same confidence that we refer to a solid, such as a lump of iron, or a liquid such as water, as forms of matter. The only consideration that affects the

chemist in this case is the purely practical one of difference in methods of manipulation which, when dealing with gaseous matter, at first presented difficulties not met with when dealing with solids or liquids; and the early history of our science will be found to contain most instructive records of the groping after the truth not only that gases were to be considered material substances, but that there were different kinds of gases or " airs " as distinct from one another as iron from chalk, or as chalk from sulphur. The difficulty arose, of course, from the circumstance that gases such as oxygen, nitrogen, and carbon dioxide, being all colourless, transparent, and invisible substances, do not directly reveal to our senses their individual characters or specific properties. The modern student learns at a very early period to distinguish between such gases, a jar of oxygen, for example, causing a splinter of glowing wood thrust into the gas to burst at once into flame owing to its energetic character as a promoter of combustion, while nitrogen and carbon dioxide extinguish flame. The latter gas also has the property of producing turbidity in a clear solution of lime in water, which property is not possessed by either oxygen or nitrogen. And, as his experience increases,

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the student will become acquainted with various other gases to which diagnostic tests can be applied, some, which burn in the air, being said to be combustible, and others possessing characteristic colours and odours, and so forth.

Admitting, therefore, once and finally, that the physical state of aggregation of matter is of secondary importance to its study from the chemical point of view, we may now pass on to the consideration of some of the other characteristics of chemical change. In many of the cases already referred to, such as the combination of iron with sulphur or with iodine—which, it will be remembered, requires the application of heat in the case of sulphur, and which takes place spontaneously in the case of iodine—the condition laid down for the production of a new and homogeneous product was that the materials should be brought together *in certain proportions* (p. 42). A quantitative notion of chemical change is thus introduced; and with this notion the student of Chemistry must become thoroughly imbued. When chemical change occurs, either as the result of combination, or of decomposition, or by any other of the processes known to chemists, it is found that the actual quantities of matter concerned in the change

bear a definite relationship towards each other. Herein will be found one of the prime characteristics of chemical change as distinguished from mechanical mixture. It is obvious that, in a mixture, there is no such restriction with respect to quantities. Gases, liquids that are miscible, and solid powders may be mixed together in any proportions, and the product partakes of the character of its components. The chemist is concerned, therefore, not only with the quality, *i.e.*, the specific properties of the substances, but also with the relative quantities of the materials which undergo transformation.

In physical terms, quantity of matter means mass; and for practical purposes the most convenient measure of mass is the gravitational measure—weight. In dealing with gases, and, under certain circumstances, also with liquids, the bulk or volume is a convenient measure; but in such cases the volume measure is generally for ultimate purposes expressed in terms of weight. The reader who studies the history of Chemistry will learn that our science only began to take rank as an exact science from the time when chemical change was studied quantitatively by means of that delicate weighing machine known as the chemical balance.

The process of weighing, the description of the balance, and of the standards of weight in use, are all dealt with in works on practical Physics and practical Chemistry; and every student is now familiarized with weighing operations at the outset of his practical work. The chief points which the general reader must realize are that the weighings carried out by the chemist are with smaller quantities, and with a degree of precision unknown to those who are accustomed only to the comparatively rough scales or weighing machines in ordinary use. For scientific purposes, also, the metric system of weights and measures is universally employed. In this system the standard of length is the metre, equal to 39·37 inches, and the unit of weight is the gram, which is the thousandth part of a standard mass of metal (platinum) kept in Paris, and known as the kilogram. The kilogram of pure water at its maximum density of 4° Centigrade occupies a volume of 1000 cubic centimetres (one litre), so that the unit weight of one gram is the weight of one cubic centimetre of pure water at 4°. Those who are familiar only with our cumbrous English system of weights and measures will acquire more definite notions when it is pointed out that the gram is equal to 15·43

grains, the kilogram to 2·2 pounds, and the litre to 61·03 cubic inches = 0·22 gallon. In ordinary quantitative chemical work, we seldom deal with quantities exceeding 100 grams—generally with much less, and a good chemical balance will weigh accurately to 1-10,000th of a gram.   Such refinement in the process of weighing would have appeared incredible to the early pioneers of quantitative chemistry, whose most accurate operations in the eighteenth century were carried out with balances which would now be regarded as relatively coarse.

The Definiteness of Chemical Change.—By means of the balance the results of chemical transformation can, therefore, be followed quantitatively.   In stating that the material or materials which undergo such change bear a definite quantitative relationship towards each other, it is meant that, when a new substance is formed or when substances arise from the combination or from the decomposition of other kinds of matter, the relative weights, both of the original materials which undergo transformation and of the new product or products, are always constant for each particular kind of matter.   Since combination and decomposition are generally reversible processes, it will be simpler at this stage to consider

combination only. From this point of view the actual weight of one substance which can combine chemically with another substance to produce a different kind of matter is as much a specific chemical property of the substance as any other character. The only qualification that must be borne in mind is that different substances may have the property of combining with each other in more than one proportion by weight; but this fact does not contravene the principle of definite combination—it only enlarges the definition of the principle so as to include more than one possibility.

An example illustrative of the foregoing statement has already been furnished in the case of iron (p. 23). It will be remembered that this substance forms " scale " when the heated metal is acted upon by water or air, and rust when it is exposed to moist air at ordinary temperatures. Now, iron " scale " and iron rust (when dry) consist of the same two substances, iron and oxygen, so that we have here two dissimilar compounds arising from the combination of the same two materials. There is, of course, no mystery about this; the balance can be made to prove that the difference is due to the fact that, in " scale," the iron and oxygen are present in

different proportions from those in which they are present in rust. And, in order to render the story more complete, it may be mentioned that we know a third compound containing only iron and oxygen which is easily obtainable by chemical methods, and which is quite distinct as a form of matter from both scale and rust, and in which the proportions of iron and oxygen are again different. Since compounds formed by the combination of oxygen with other substances are generally known in Chemistry as *oxides*, the case will be made more definite by stating that there exist three oxides of iron—three different substances all arising from the combination of the same two materials in different proportions. It is quite easy to ascertain by methods which must be considered hereafter the relative proportions of iron and oxygen contained in the three oxides ; and it will give greater precision to the notion of chemical transformation in its quantitative aspect if it is stated that the iron oxide of rust contains 70 per cent. of iron, the iron oxide of " scale " 72·4 per cent., and the third oxide 77·8 per cent. of iron.

The main principle—the definiteness of chemical change—is thus upheld, because whenever iron is made to combine with

oxygen, directly or indirectly, we always get one or another of these three substances. There are no definite intermediate substances; the definiteness is chemically rigid. It is a chemical truth expressed in numerical terms that cannot be tampered with. If it were desired to produce a substance containing iron and oxygen in some other proportions than those indicated, it could not be done by chemical means, but only by making a mechanical mixture of some or all of the three oxides to each of which Nature has attached the brand of individuality.

It will now be understood why the production of a definite homogeneous substance by chemical change is conditioned by the relative quantities of the materials brought into combination. The relative weights of the materials which combine being fixed in the sense indicated, if too much or too little of one of the components is used the product of the transformation is necessarily a mixture consisting of the new compound, *i.e.*, the chemical product, *plus* the excess of unchanged material. For example, the compound formed by heating iron with sulphur (p. 39) is a *sulphide* (note the analogy of the term with *oxide*) of iron containing iron and sulphur in the ratio 4 : 3. If more iron is put into

the original mixture, the product would consist of the sulphide mixed with the excess of unconverted iron. Again, the iron *iodide* formed by the direct union of iron with iodine (p. 38) is a product resulting from the combination of 7 parts by weight of iron with 31.7 parts of iodine. These materials cannot be made to combine in the chemical sense in any other proportions; any excess either of iron or of iodine would be left uncombined, and could be separated from the mixture by appropriate methods.

The very definiteness of chemical change thus prohibits a gradual transition from one form of matter to another. There is necessarily an abruptness about the transformations; there can be no half measures— each material must have its full complement of its associated material. If it is not supplied with as much as it can combine with, there is a residue of unappropriated and unchanged material. In speaking of chemical change as abrupt, it is not meant that the transformation takes place suddenly. There are chemical changes of every degree of velocity, from a practically instantaneous explosion to a transformation which may take days, weeks, years, or geological periods. Direct combination is generally, but not invariably, a rapid process.

But, whether rapid or slow, the definite character of chemical change is universally maintained. Indeed, the measurement of the velocity or rate of chemical change is only made possible in those cases where it is measurable by the definiteness of the result, because the quantity of chemically transformed material (as distinguished from the unchanged material) which is produced at measured intervals of time can be determined either directly or indirectly by means of the balance.

Some of these points are illustrated by the examples of chemical change already cited. Thus, the rusting of iron is a slow process; the conversion of iron into " scale " by the action of water or oxygen upon the heated metal is a sudden change. When a mixture of iron and sulphur is heated to the point at which combination takes place, the whole mass suddenly glows, and the conversion into sulphide is so rapid that it may practically be considered to be instantaneous. In some cases, both of slow and of rapid change, it has been observed that the final stage is reached through a series of intermediate steps, but the definiteness of the transformation is not in any way interfered with—each stage is as definite as its successor; it is simply a

case of a definite, stable, final stage being reached through one or more unstable but equally definite intermediate stages. In some cases it is possible to arrest the process at an intermediate stage, and to isolate the intermediate product. The latter is in all cases the result of combination (or of decomposition) in as definite proportions by weight as is the final product—the end result. In other words, the course of the chemical change can in many cases be followed through successive phases, each perfectly definite; and it has accordingly been suggested with much plausibility that all chemical change takes place in stages, these stages in the majority of cases being passed through too rapidly to enable them to be detected by our present methods. Chemical change has thus been aptly compared to a drama, the scenes of which are shifted with great rapidity, the spectator seeing only the final act. Applying this metaphor to the present discussion, the main point to be borne in mind is that each scene in the drama—even if passed through with explosive velocity—is a perfectly definite picture from the chemical point of view, although the eye of the chemist may not at present be capable of appreciating it. A great step in the development of the

science of Chemistry will have been made when new methods are discovered or known methods applied to the study of what may be called transition phases.

The Conservation of Mass.—It will have been made evident to the reader that, although chemical change is characterised by those general criteria which have been discussed, there is still an individuality about the process which makes it essential both for scientific and for practical purposes to study particular cases in detail. It is, in fact, by such detailed studies that our generalized statements have been made possible. The vastness of the prospect thus opened out to the gaze of the student of Chemistry will now begin to loom. Before proceeding to further developments, however, there yet remains an aspect of chemical change of fundamental importance which the student will be brought to face at the very beginning of his studies. It will have been realized that Chemistry is concerned with the transformations of matter, and that these transformations are, so far as concerns the relative masses of the materials which undergo transformation, of a perfectly definite character. It is but another step to the conclusion—based, of course, upon experimental evidence—that during such trans-

formations there is neither gain or loss of material. This is tantamount to the proposition that matter is indestructible by any known chemical process. There is profound modification or transformation as the result of chemical change, but the whole quantity of matter, *i.e.*, the mass, remains constant ; the sum total of the weights of the materials employed is the same at the end of the transformation as it was before the change occurred. Seven unit weights of iron heated with four unit weights of sulphur give eleven unit weights of iron sulphide with the arithmetical accuracy expressed by $7 + 4 = 11$, and so on for all other cases of chemical change, either by combination or by decomposition. If, for example, the above process could be reversed (as it can by indirect methods), and the iron sulphide resolved into its components, eleven parts of the sulphide would give seven parts of iron and four of sulphur or, arithmetically, $11 = 7 + 4$.

The statement that you only get out of a given weight of matter as much as you start with may appear at first sight such a self-evident proposition that no special proof need be adduced. But there is a deeper significance in the statement than might be imagined on superficial consideration. In the first place,

it involves the great principle that matter can neither be created nor destroyed by chemical agencies. In the next place, it opposes what might be considered the common-sense view that such deep seated and startling transformations as are wrought by chemical change must necessarily be accompanied by loss or gain of material. That such a view should have been entertained in former times is not surprising when it is remembered that the truth of the doctrine can only be demonstrated when *all* the products of the change are collected and weighed. If, as is often the case, one of the products is gaseous and escapes in an invisible form, it is understandable that, at a time when the material nature of gases had not been thoroughly recognized, it should have been believed that chemical change might be accompanied by a destruction of matter. Although the scope of this work does not admit of the historical treatment of the subject, it must be recognized as marking an epoch in the history of Chemistry, that the conversion of the scientific world to the doctrine of the indestructibility of matter was brought about mainly by the researches of the illustrious French chemist Lavoisier (1743-1794), who fell a victim to the Revolution. The student of the history

of our science will learn that, although the materials for the establishment of this doctrine were in hand, its acceptance had been retarded by the prevalence of certain erroneous theoretical views which were only finally overthrown by the experiments and reasoning of Lavoisier and his disciples.

A principle so fundamental as that of the indestructibility of matter, which now permeates every branch of science, must enter into the mental constitution of the would-be chemist. Through every phase of chemical change it is known that this principle holds good, although in ordinary practical work it is never realized unless the most refined methods are employed for ascertaining the weights of all the products. In every-day laboratory or factory experience, there is always more or less loss due to the imperfection of methods; and the theoretical ideal that the sum total of the weights of the final product or products is equal to the sum total of the weights of the initial materials is seldom realized. But the loss arising from unavoidable manipulative causes no longer shakes faith in the doctrine, although, for certain philosophical reasons, it has been thought necessary to retest its truth with the utmost refinement of modern scientific resources.

Water a Chemical Compound.—In the light of these principles—the definiteness of chemical change, and the indestructibility of matter —all chemical transformations may be considered and illustrative examples multiplied indefinitely. One other case may be introduced at this stage, both on account of its historical interest and because it will enable fresh materials to be added to the small store of facts which have thus far been found to furnish a sufficient basis for the discussion of the broader generalities. Attention is invited to another very familiar substance, water, which, since it forms iron scale when brought into contact with the heated metal (p. 23), may be considered to have been proved to be a substance containing oxygen. The question whether the oxygen in air and water may not be present in a different condition in the two substances has already been raised (p. 27). Air has been proved to be a mixture; water has been proved to contain oxygen, and, since water differs so fundamentally from oxygen in all its properties, chemical and physical, it is evident that it must contain something in addition to oxygen. What is that other constituent, or what are the other constituents if more than one; and is the oxygen simply mixed with the other con-

stituent or constituents, or is it chemically combined ? The answer to these questions will furnish further instructive illustrations of facts, methods, and principles.

The fact that heated iron takes oxygen out of water suggests the use of this metal in order to find out what is left after the oxygen has been removed. In forming iron scale by plunging red-hot iron into water, it might be noticed that with the escaping steam there is a gas which, unlike the steam, does not condense on cooling. This gaseous product of the action of water upon hot iron is not easy to detect by such a rough and ready experiment ; but by a refinement of method, and without in any way interfering with the principle by altering the materials, this gas can be readily obtained in any desired quantity. In practice, instead of using water, we use steam, which is the same substance in a different state of physical aggregation ; and the iron, in coarse fragments, such as wire or nails, is enclosed in a tube of porcelain or any suitable material that will stand the heat. The steam is passed through the heated tube, and the emergent gas collected by appropriate methods in any suitable vessel. At the end of such an operation, the iron will be found to have been more or less converted

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into scale ; and the new gas, on comparison with oxygen or nitrogen, will be found to possess quite different properties—it is a different kind of gaseous matter. This gas is known as hydrogen ; like nitrogen or carbon dioxide (p. 36), it is colourless and transparent, and it extinguishes flame, but, unlike these gases, it is combustible, burning in the air with a barely perceptible, but very hot flame. Hydrogen is the lightest form of matter known on this earth, being, bulk for bulk, $14\frac{1}{2}$ times lighter than air, 16 times lighter than oxygen, and 11,000 times lighter than water. In view of this fact, the gas is difficult to deal with practically, since it tends to escape from all vessels, tubes, joints, etc., having the slightest porosity.

Water is thus shown to contain hydrogen as well as oxygen ; and, since by no physical process, such as diffusion (p. 56), is it possible to separate hydrogen from water, it is evident that the gas is chemically combined. The question whether the oxygen in air and water may not be present in different states is thus definitely answered. Moreover, a mixture of hydrogen with oxygen is not water, but a gas intermediate in properties between its two components. The oxygen in water is chemically combined, and its separation by

hot iron is a chemical process. It will be noticed that the removal of oxygen from water by iron differs materially as a process from that which takes place when iron rusts in air : in the first case the iron has to be red-hot, while in the second case the combination takes place at the ordinary temperature. Chemical combination has to be overcome in the case of water, and not in the case of air, which is simply a mixture.

From this illustration we can develop further the principle of preferential combination (p. 35), because there are other metals besides iron which liberate hydrogen from water, while many other metals exert no such decomposing action. Thus, a familiar metal, zinc, when heated in steam liberates hydrogen at a lower temperature than iron, and another less familiar metal, magnesium, at a still lower temperature; while some metals, which are not generally familiar, and which will be afterwards referred to, will decompose even liquid water and liberate hydrogen at the ordinary temperature. So we could construct a graduated scale of preferences for oxygen as measured by the temperature at which the hydrogen is liberated from water. On such a scale the inverse preferential order would be iron, zinc, magnesium,

and then those metals which decompose cold water.

Then again, as already stated, some metals do not liberate hydrogen from water at all, although they are capable of combining with oxygen. Such a metal is the familiar substance copper, which, like iron, when heated unites with oxygen to form an oxide, a black substance totally unlike the red lustrous metal and the gaseous oxygen from which it is formed. The removal of oxygen from the air by passing the latter through a tube containing heated copper is one of the recognized methods of obtaining nitrogen. These facts furnish further proof of water being a chemical compound, because one metal (iron), which has a sufficiently strong liking for oxygen to combine with this substance at the ordinary temperature, has to be made red-hot before it can take the oxygen out of water, while another metal (copper), which has sufficient liking for oxygen to form an oxide when heated in contact with that gas, fails to remove the oxygen from water even when red-hot. From which facts it follows, also, that on the inverted scale of preferences for oxygen given above, copper would precede iron.

And now there remains to be answered

the question whether water contains anything besides oxygen—a question which, of course, relates only to water as an individual form of matter, and not to water as we find it in nature, in rivers, or in rain, or in the sea, because such water always contains other substances dissolved in it. Natural water is, in fact, an aqueous solution of substances derived from the air and the earth through which it percolates. When a liquid like water takes up other substances, either solid, liquid, or gaseous, and forms a homogeneous mixture, the latter is technically described as a *solution*; the water in this case is described as the *solvent* and the other (dissolved) substances as the *solutes*. This point is raised in a preliminary way now, in order that it may be realized that we are at present concerned only with water, and not with any adventitious matter that it may contain. Returning now to the initial question, and referring to the statement that a mixture of oxygen and hydrogen is not water, it only remains to be added that a mixture of these gases explodes when a flame is applied, and the product has been found to be water and nothing but water. This is an old and now a well known fact, but the reader must again be reminded that a discovery of this

importance was made only by skilful experiment carried out with all the refinements of method available at the time by Cavendish (1731-1810). In practice, the gases are enclosed in a strong glass vessel (eudiometer) with platinum wires sealed through the side, so that the explosive combination may be brought about by passing an electric spark through the mixture.

Since oxygen and hydrogen give nothing but water when combined, the question is therefore answered—water as such contains no other form of matter. So that, as the result of chemical transformation, a gas, hydrogen, of which the boiling-point is about 252° below the freezing-point of water, in combination with another gas, oxygen, of which the boiling-point is about 183° below the freezing-point of water, gives a liquid 1,400 times denser than hydrogen and boiling at 100° above the freezing-point of water. The profound nature of chemical change is again exemplified; but its definiteness has not yet been made apparent in the case under consideration. Supposing, then, that into a suitable vessel, such as a strong glass tube graduated by marked divisions which enable us to measure the volume of gas, and having wires sealed through to enable an electric

spark to be passed, we introduce hydrogen and oxygen in known volumes. It is not easy —speaking strictly it is impossible—to form an accurate notion of the method of conducting such an experiment as this by simply reading a description of it. The student of Chemistry, however, learns how to manipulate gaseous matter with the same facility that he deals with solids or liquids, and the methods are given in practical works on the subject. But the principle is quite intelligible, for we have only to consider that we have a mixture of hydrogen and oxygen in which the actual volume of each gas is known. The mixture is exploded by an electric spark, and some of the gas disappears when the vessel has cooled down. In other words, there is shrinkage of volume, because the water which is formed, being liquid at ordinary temperatures, condenses to a dew on the inside of the vessel. But the whole of the gas does not disappear in an experiment of this kind; there is always a residue, and, by testing that residue, it is easily shown that it is either oxygen or hydrogen, according to the proportions of the gases in the original mixture. By such observations it is found that, for every unit volume of oxygen, two unit volumes of hydrogen disappear, or conversely, that for every unit

of hydrogen half a unit volume of oxygen disappears.

Hereby is once more illustrated the definiteness of chemical change ; under the conditions imposed, the gases refuse to combine in any other proportions—there are no intermediate proportions ; it is two to one, or nothing. Any excess of either gas over and above these proportions is left uncombined, and that is why in such experiments there is always some residual gas ; it is only when a mixture of exactly two volumes of hydrogen with one volume of oxygen is exploded that there is no gas left—the sole result of the combination is then water, and the vessel in which the explosion takes place is found to be practically vacuous when cold, because the condensed water occupies but a very small volume. The definiteness in this case manifests itself volumetrically, but that is really the same thing as definiteness by weight, because the gases have perfectly definite weights as compared with each other under comparable conditions, the relative weights of equal volumes of oxygen and hydrogen being about $16 : 1$. As one volume of oxygen combines with two volumes of hydrogen, the relative weights of the two substances contained in water are accordingly $16 : 2 = 8 : 1$.

Other methods of determining the composition of water are well known, but these involve new principles, and cannot be discussed now. The chemical change which takes place when hydrogen and oxygen combine is, like all other chemical changes, a redistribution or rearrangement of matter, but the weight of the materials remains constant—the principle of the Conservation of Mass is maintained. If the vessel containing the gases is weighed before and after the explosion, there will be found neither loss nor gain—a fact which in this instance is made more striking because of the total disappearance of the gases as such when the mixture contains the correct proportions.

The principle of the Conservation of Mass, which lies at the root of the science of Chemistry, will remind the student of Physics of the analogous principle of the Conservation of Energy. To the chemist, this last doctrine is of equal importance with the first, but the reader must beware of straining the analogy between the two doctrines. The different forms of energy are interconvertible, but it by no means follows that different forms or kinds of matter are interconvertible. Were such interconvertibility possible, we should have realized " transmutation " as distin-

guished from transformation. Transmutation was the moving principle prompting the work of the old alchemists, gold being the form of matter striven for. It is now recognized that alchemy failed in this particular quest, and the idea of transmutation passed out of Chemistry when it became a science. In modern times, and in the light of new discoveries, the idea has been reinstated in another form, and there is some evidence in its favour—how much is a matter of judgment and a question for future investigation. But all this belongs to another story which cannot be narrated here, and the reader must be referred for further information to works dealing with Radioactivity, or to the volume on " Matter and Energy " by Mr. F. Soddy, in this series.

CHAPTER IV

ELEMENTARY AND COMPOUND MATTER — THE
CHEMICAL ELEMENTS—METALS AND NON-
METALS

Elementary and Compound Matter.—Matter is
comprised under the general term " stuff,"
an expression which finds its equivalent in
the German *Stoff*. Thus we speak of food-
stuffs, dyestuffs, etc., and the German for
hydrogen, *Wasserstoff*, indicates, like the
Greek roots of the English name for this
substance, that it is the stuff from which water
is produced. For the purpose of illustrating
the nature of chemical change, appeal was
made in the preceding chapters to a number
of well-known things, such as air and water,
iron, sulphur, iodine, sugar, charcoal, and
chalk. By the chemical study of some of
these " stuffs," we have been made acquainted
with their less familiar components, such as
the gases oxygen, hydrogen, and nitrogen,
which do not come within the popular notions
of matter unless attention is specially directed

to their material nature. It is obvious that many of the substances referred to are compounds made up of at least two kinds of matter, such, for example, as iron rust and iron scale composed of iron and oxygen, iron sulphide made up of iron and sulphur, or water composed of hydrogen and oxygen.

It thus falls within the province of Chemistry, which is concerned with the transformations of matter in the sense which has now been made clear, to determine, in the first place, whether a substance which is not a mixture is composite—whether other forms of matter can be got out of it by chemical or physical processes. It may be well to take advantage of this opportunity for pointing out that to the chemist the various forms of energy, heat, light, electricity, etc., are as much chemical agencies as matter itself, in so far as these forms of energy are capable of producing chemical change. We investigate the composition of matter both by physical processes and by purely chemical processes, meaning by the latter the action of one form of matter upon another. This last case is also ultimately resolvable into terms of energy ; but for the present the distinction will be found convenient. The study of the composition of matter can be conducted in two ways—

a substance may be resolved by physical or chemical means into its components, or the components may be brought into combination, and the substance built up.   The first process is, in a general way, described as *analysis*, and the complementary process as *synthesis*.   Very often the composition of some particular stuff is proved in both ways.   Thus, when water is shown by the action of hot iron to contain oxygen and hydrogen, its composition is proved by analysis ; when water is formed by the combination of oxygen and hydrogen, its composition is proved by synthesis.   The more complex the substance—the greater the number of different forms of matter which enter into its composition—the more important and, it may be added, the more difficult does the proof of its composition by both methods become.   In the case of extremely complex substances, it is often not possible in the present state of knowledge to complete the synthetical evidence ; but, as we are approaching the subject gradually, it will be advisable at this stage to concentrate attention upon the simpler cases.

For at least a century and a half, chemists have thus been trying by every possible method to pull all available materials to pieces. The component parts which the chemist has

striven for are not simply proximate, but ultimate—as ultimate as his methods can carry him. The mineralogist, for instance, by microscopic examination or by other methods, can determine the proximate components of a mineral—he may resolve granite into quartz, felspar, and mica ; the biologist may dissect an animal or a plant into various organs and tissues, and, by pushing his studies still further into the domain of cytology, he may study the individual cells of which all organisms are composed, and, by the application of the highest magnifying power and the use of dyes which stain the different component materials of the cell selectively, he may effect a microscopic analysis of even the minutest organized units of animals and plants. Or the mechanic may separate a machine into its component parts to find out how it works, and he may put the parts together again and restore the mechanism to its working condition ; his analysis need go no further for his purpose than the separation of wheels, cranks, levers, and so forth. But the chemist pushes his inquiries deeper than this ; he can tell the mineralogist what the components of granite are themselves composed of, he can supply the biologist with information concerning the different complex forms of matter of which

the organized units are composed, and he can resolve the component parts of a machine into a few metals, upon the specific properties of which the efficiency of the machine depends.

The general result of the study of matter from this chemical point of view has been the discovery that the process of resolution in every case reaches a limit.   From whatever materials we set out, there are finally obtained some forms of matter which cannot be further decomposed—from which nothing different can be produced by any known process of resolution ; substances whch are said to be elementary.   So that from the chemist's standpoint all matter is either resolvable or unresolved; the Universe is built up of elementary and compound matter.   Whether elementary matter is in its ultimate nature unresolvable is a question for the future to decide ; the point is raised in connection with recent researches in Radioactivity.   But for all practical purposes it may be assumed that, whether further decomposition of elementary matter is possible or not, no such resolution takes place in the course of any ordinary case of chemical change.

The Chemical Elements.—The component parts of anything may, therefore, be said to be its elements, the degree of resolution

depending very much upon the particular branch of science. Thus, to the anatomist, the limbs, organs, skeleton, etc., are the elements of an animal; the bones are the elements of the skeleton; the histologist separates tissues into elementary cells; and to the cytologist the various components of the cell constitute its elements. Or, to the engineer, the wheels, cranks, etc., of a machine are its elements. The separation of matter by chemical methods is evidently more fundamental; and the chemical elements are recognized in every department of science. The evolution of the idea of an element in Chemistry forms an interesting chapter in the history of the science, and the student will find the story most fascinating. It will be readily understood that, with the discovery of new methods of decomposing matter chemically, substances apparently elementary were resolved. In this way, the list of elements was from time to time revised by the substitution of new elements for their previously unresolved compounds. Then, again, with increasing activity in the study of rare minerals and out-of-the-way materials—with refinement of methods of separation, and with improvements in physical and chemical methods of detection and discrimination—

the number of elements has been increased until at the present time about eighty—according to the latest census eighty-two—of these unresolved " stuffs " are known. When the reader hears of " new " chemical elements being discovered, he will, of course, understand that what is really meant is the detection of some element that had previously escaped notice by virtue of its rarity, or on account of its being difficult to separate from associated matter, or because of its lacking obtrusively distinct characters. No chemist has ever done more than bring to light those raw materials of the Universe which were already in existence ages before the advent of man upon this earth.

It is the business of the chemist to know as much as possible about these elements ; to acquaint himself with their mode of occurrence in nature, with the methods of isolating them, and with their characteristic properties as individual forms of matter—in short, with their natural history. The student need not be appalled at the magnitude of the field thus opened out ; he will not be called upon to commit to memory long tables of facts and figures—all has been systematized and simplified by scientific generalization. The chemical elements play very different parts in the

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economy of nature, and in their utility in the
arts and manufactures. Some are abund-
antly distributed both in the free and combined
state; others are also abundant, but occur
only in combination; others are rare in the
free state, while their compounds are common;
and others, again, are extremely scarce in any
state. It is not proposed, even if it were
possible, in this little volume to set forth more
than a few generalities concerning the eighty-
two elements known to science, since any
invidious selection would necessarily convey
a false impression of relative importance. In
applied chemistry, in the economy of life,
in their capability of forming multitudinous
compounds, every set of elements has its order
of importance; in the light of pure science,
there is no absolute scale of importance;
every element has its own story to tell, and
one which occurs only in infinitesimal traces—
the newly isolated radium—has opened up
some of the most fundamental questions
concerning the ultimate constitution of matter
that have ever been raised since the individ-
uality of the elements became a recognized
scientific doctrine.

Acquaintance with some of the chemical
elements has already been made in the pre-
ceding chapters; and it will have been

realized that the conception of an element as an unresolved form of matter is quite independent of the physical state of aggregation. Thus, oxygen, hydrogen and nitrogen are gaseous elements under ordinary conditions; sulphur and iodine are solids. Iron, copper, zinc and magnesium are all elements, and have been mentioned as belonging to the category of metals—they are metallic elements, and are all solid at ordinary temperatures, but have definite points of liquefaction, *i.e.*, melting-points. The familiar metal mercury, or quicksilver, is an element that is liquid under ordinary conditions, but it solidifies at $-39 \cdot 5°C.$, and is a colourless vapour above 357°. It would be possible to make a classification of the elements based on their physical state as familiarly known to us; but nothing would be gained by such a classification beyond mnemonical assistance. Chemical classification naturally goes deeper, and is directed towards the establishment of chemical relationships—the association of elements which are allied in their chemical characters. Solid sulphur and gaseous oxygen, for example, have many chemical properties in common. No classification of the elements based on any set of purely physical characters is of any use from the chemical point of view, although,

as will be seen subsequently, the chemical classification is of the greatest value from the physical point of view.

The reader is invited to consider another example which will serve to introduce a set of four closely related elements, one of which, iodine, has already been made use of in illustration of chemical change (p. 38). Of these four elements, the most abundant is chlorine, which is a component of common salt ; and, as common salt is contained in and was originally obtained from sea water, the group has received the name of *Halogens*, which simply means generators of salt like sea-salt. The halogens, then, are fluorine, chlorine, bromine and iodine. Fluorine occurs in combination as a constituent of the minerals fluorite (fluor spar) and cryolite, the other constituents of these minerals being certain metallic elements which may stand over for further consideration. Chlorine occurs in combination in common salt, vast deposits of which are found " bedded " in certain geological strata ; this salt is also the main component of the solid residue left by the drying down (evaporation) of sea water. Bromine also is found in combination as a salt in the same geological deposits with common salt ; and iodine is found in combination in the

earthy residue or ash left when sea-weeds are burnt. There are also found in Chili deposits of a certain salt known as Chili Saltpeter, which is largely used as a fertilizer for crops; with this salt certain compounds of iodine are found in admixture. Thus, the halogens are found in nature only in a state of combination; they have been " discovered," *i.e.*, isolated, by chemical methods, and their elementary character has been established by chemical research. The question now arises— why are these four elements grouped together ?

That the classification is independent of physical considerations is shown by the fact that fluorine and chlorine are gases at ordinary temperatures, bromine a deep red heavy liquid, and iodine a metallic looking solid. The relationship between the members of this family is primarily chemical; with the same element they form compounds of absolutely similar types and characters. To simplify matters at this stage, it may be considered that the element which is most commonly found in combination with the halogens under natural conditions is the metallic element known as *sodium.* Common salt is a compound of chlorine and sodium; and, just in the same way that we speak of compounds of oxygen as oxides (p. 71), we

say that salt is sodium chloride. The other halogens form similar compounds—sodium fluoride, bromide and iodide respectively. It may be mentioned incidentally that fluorite is a compound of fluorine with another metallic element, *calcium*, of which quicklime (p. 39), is an oxide ; while cryolite contains, in addition to the fluoride of sodium, the fluoride of the metallic element *aluminium*, of which element the mineral substance clay is one of the most familiar compounds. Now, all the sodium compounds of the halogens are alike in their general properties ; they are all colourless salts, crystallizing in the same cubical form, and having the same chemical characters. What is true for sodium is true for calcium and for other elements, metallic or non-metallic, so far as concerns the similarity of the four compounds in each set. Thus the four halogens form a series of four compounds with hydrogen, all colourless gases at ordinary temperatures, and all having similar chemical properties ; the fluoride, chloride, bromide and iodine of hydrogen are as comparable among themselves as are the sodium compounds.

Thus, in the halogens we have a natural group or family of elements which are associated together because of their chemical

relationship. The profound significance of chemical relationship will be more and more realized as the student becomes more and more familiar with the natural history of the individual elements. All the elements can be grouped into families, the members of which possess among themselves certain characters in common. Such classification is the first step towards the systematic study of the elements as a whole. It is unnecessary now to adduce other illustrations; but this same group will enable us to lay hold of another principle of great importance—the principle of gradation of character. To the chemist, this means gradation of chemical character. We can, for instance, arrange the halogens in a series in the order of their chemical activity. Some notion of what is meant by chemical activity has already been given (p. 83). The order from this point of view is (1) fluorine, (2) chlorine, (3) bromine, (4) iodine. Fluorine is the most energetic, iodine the least; fluorine combines so energetically with other elements, and forms such stable compounds, that it is one of the most difficult elements to isolate, the difficulty arising from the circumstance that it attacks all the ordinary materials of which chemical vessels are made; and its isolation was only made possible by using

an apparatus constructed of the metal platinum, which is so inert towards all the chemical elements that it resists the attack of the intensely active element (Moissan, 1886). The relative activities can be illustrated by the statement that fluorine decomposes chlorides, bromides and iodides, turning out the halogen from these compounds and forming fluorides ; chlorine similarly displaces bromine and iodine ; and bromine displaces iodine.

From considerations of this sort we are thus enabled to form the graduated series given above. Having formed this series on chemical grounds, then, physical properties reveal themselves as also gradational. Take the boiling-points for example : fluorine, $- 187°$; chlorine, $- 35°$; bromine, $59°$; iodine, $184°$. Or the melting-points : fluorine, about $- 223°$; chlorine, $- 102°$; bromine, $- 7·3°$; iodine, $114°$. Or the colour : fluorine, pale greenish yellow ; chlorine, deeper greenish yellow ; bromine, deep red ; iodine, violet vapour. From such facts as these—and other chemical families also show gradation of characters—it follows that chemical relationships are expressive of some deep-seated properties inherent in the ultimate constitution of matter. What these ultimate properties are may be brought to light by future research ; in the present state

of knowledge we simply deal with them as they are presented to us. The gradation, as will be seen later, is also associated with another fundamental attribute, mass, as measured by weight; but this belongs to another chapter in which the classification of the whole body of chemical elements has to be dealt with.

It will be now seen that there is justification for the statement made above that the chemical classification of the elements is of importance in Physics, because in a graduated series the physical properties can be inferred within certain broad limits from the position of the element in the series. Thus, knowing the boiling-points of fluorine and bromine, it could be predicted that the boiling-point of chlorine would lie somewhere between, or, knowing the descending order of boiling-points from iodine to chlorine, it could have been foreseen that the boiling-point of fluorine, when determined, would be found to be the lowest of the series. Still more potent as a scientific weapon would be any larger scheme of classification which comprised all the smaller natural groups of elements, and enabled the prevision of properties to be made with a greater degree of accuracy—with a precision measured by narrow instead of by broad

limits. That such a scheme exists will be made clear in a later chapter.

Metals and Non-Metals.—In the course of the preceding section, a general grouping of the elements has tacitly, if not explicitly, been adopted. Several elements, such as iron, copper, zinc, magnesium, sodium, calcium, and aluminium, have been spoken of as metals. It is customary to speak of the elements as metallic or non-metallic—as metals or non-metals. Here again, we have a classification in which chemical properties are expressive of some correlated physical distinction between the groups. It is not possible to draw a hard and fast line between the two divisions; but in a general way, and as the result of even the most casual observation, the reader cannot have failed to have associated certain characters with the term metal. Of course, many familiar metals are not elementary, but mixtures—so-called alloys—or, to speak more accurately, either simple mixtures or solid solutions of two or more elementary metals. Brass, for instance, is an alloy of copper and zinc; bronze, gunmetal, and bell-metal are alloys containing the elements copper and tin, etc.; the " silver " of the coinage is not the element silver, but an alloy of silver and copper;

the " gold " of our coinage is an alloy containing 2 parts of copper in 24 parts of gold. Pewter and soft solder are alloys containing the elements tin and lead ; steel, one of the materials most widely used in constructive engineering work, is the metallic element iron containing a small percentage of carbon. The physical properties of the metals are profoundly modified by this physical association with other metallic or non-metallic elements, so that many of these alloys are of enormous industrial importance for purposes for which the pure metals would be useless. We are not specially concerned here with this branch of applied chemistry—it belongs to a large and important subject which is studied under the designations Metallurgy and Metallography, and special works must be consulted for detailed information.

From the chemical point of view, one of the chief distinctions between the two groups is to be found in the nature of the compounds which they form with oxygen—their oxides (p. 71). Of the elements already referred to, hydrogen, nitrogen, carbon, sulphur, and the halogens are non-metals. Now, these elements can all be made to combine with oxygen (which is also a non-metal)—sometimes directly, as in the case of hydrogen, sulphur, carbon

and nitrogen, and sometimes indirectly, as in the case of the halogens. All these oxides of the non-metals, however formed, are, with the exception of water, which is a neutral compound, possessed of certain properties which are described as *acid*. Their solutions in water are sour to the taste, and redden the blue vegetable colouring-matter litmus. These acids, moreover, have the property of combining with the metallic oxides by which the said acids are more or less neutralized, giving rise to the formation of those extremely important compounds known by the general name of *salts*, about which more remains to be said. The oxides of the metals are known as *bases* (in contradistinction to acids); so that the general distinction between the groups may be summarized by the statement that the non-metals form acid oxides which in aqueous solution are sour and redden litmus, while the metals form basic oxides which neutralize the acids to form salts and which restore the blue colour of litmus. Of course, the distinction is not absolute—there are some acid metallic oxides, but there are no basic non-metallic oxides. Neither must it be inferred that the property of conferring acidity exclusively pertains to oxygen, since the compounds of the halogens with hydrogen

(p. 102) are also acids, although they contain no oxygen.   But in general terms the distinction is sound ; it corresponds with the facts, and is further borne out by another distinctive character which will introduce a new set of considerations.

Beginning, as before, with a simple case, common salt may be taken as a type of the class of compounds termed salts.   It has already been stated that this substance is a compound of the metal sodium with the non-metal chlorine.   Although metallic and non-metallic oxides combine as just stated to form salts, sodium chloride is also a salt in the chemical sense, so that there may be salts with or without oxygen—haloid-salts and oxy-salts.   The various methods by which salts can be formed do not now enter into consideration ;   they can be produced by other means than the combination of acids and bases, but, however formed, they are capable of being decomposed by electricity. A salt, either in solution in water or in a state of fusion by heat—if it can be fused—is resolved by a current of electricity ; it is said to be an *electrolyte*, and to undergo *electrolysis*.   The same is true, it may be said parenthetically, of acids and bases ; these also are electrolytes.   Now, electrolysis is a

process of chemical decomposition by physical agency (p. 92) ; and the products of electrolysis are the original components of the salt, acid, or base, or the secondary products of the chemical change resulting from the interaction of the primary products and the solvent. Thus, if one of the products of electrolysis is a metal which decomposes water at ordinary temperatures, it is evident that we should not get that metal by electrolysing an aqueous solution of one of its salts, but the products of the interaction of the metal and water, one such product being hydrogen (p. 83). Sodium is one of the metals which decompose water at ordinary temperatures, so that, if a current of electricity is passed through an aqueous solution of common salt, the products are chlorine and hydrogen—not chlorine and sodium. If dry fused sodium chloride is electrolysed, the products are sodium and chlorine.

The general result is that the primary products may always be regarded as a metal and the other component of the salt, whatever that may be. If we are dealing with a solution of an oxy-salt, the products are hydrogen and oxygen. But the oxygen is in this case a secondary product, since the salt is resolved into metal (or hydrogen, if the latter decom-

poses water), and the whole oxygen-containing group, which latter group decomposes water with the liberation of oxygen. The oxygen-containing group is the electro-negative equivalent of the halogen in sodium chloride. The details of electrolytic decomposition and their theoretical explanation are dealt with in works on electro-chemistry. The main fact which this introduction is intended to bring out is that the metal and the halogen or oxygen-containing group always travel in opposite directions—the one component of the salt appears at one pole or electrode, and the other component (or the secondary products) at the other electrode.   And, in accordance with the principles of electrical science, the metal, which always appears at the negative electrode (or kathode) is said to be electro-positive, and the halogen or other acid group, which is liberated at the positive electrode (or anode), is said to be electronegative. So that there is a physical classification of the elements thus made possible according to the behaviour of their compounds on electrolysis ;   and in broad terms this classification agrees with the division into metals and non-metals, the former being as a group electro-positive, and the latter electronegative. It must be noted that the non-

metal hydrogen is an exception, since it is distinctly electro-positive. But this exception has a special significance, because, in most of its chemical relationships, hydrogen is more closely allied to the metals than is any of the other non-metallic elements ; and it would not be straining matters unduly even now to class hydrogen with the metals if only its chemical characters are taken into consideration.

Out of the whole list of elements, eighteen may be labelled non-metals. Here, again, there is an indication that chemical character is expressive of something profound and inherently constitutional in matter, because, as groups, the metals and the non-metals differ in many well-known characters. Thus, the metals are opaque (excepting when in very thin films) and, when in a massive state, as distinguished from a pulverulent condition, possessed of " lustre "—a property well exemplified by the familiar appearance of polished silver, gold, or copper. Among the non-metals, iodine is the most pronounced exception, as its crystals are possessed of distinctly metallic lustre. In contradistinction to the opacity of the metals, ten of the non-metals are transparent gases at ordinary temperatures. The metals as a class are,

in varying degrees, conductors of heat and of electricity, while the non-metals are bad conductors or non-conductors. Among the solid non-metallic elements, such metallic properties as malleability or tenacity are not met with.

With respect to the distribution of the elements, it is of interest to note that more than three-fourths of the accessible crust of this globe upon which we live is made up of the two non-metals, oxygen and silicon, about one-half being oxygen. Nothing affords more striking evidence of the marvel of chemical change than the contemplation of this geo-chemical fact, that the superficial " solidity " of the earth is due to the predominance of those mineral constituents into the composition of which gaseous oxygen and the non-metal silicon enter to a preponderating extent. The whole crust of the earth with which geology deals is composed to the extent of more than 99 per cent. of only about twenty out of the eighty-two elements. This will give an idea of the rarity of some of the materials which the chemist has had to deal with. Out of the twenty elements which predominate in the earth's crust, four non-metals and seven metals exist in quantities which have been estimated to constitute more than 99 per cent.

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of the whole crust in the proportions by weight given below (F. W. Clarke) :—

Oxygen,* 49·98 ; Silicon,* 25·3 ; Aluminium,† 7.26 ; Iron,† 5·08 ; Calcium,† 3·51 ; Magnesium,† 2·5 ; Sodium,† 2·28 ; Potassium,† 2·23 ; Hydrogen,* 0·94 ; Titanium,† 0·3 ; Carbon,* 0·21.

The actual mode of combination of the chemical elements as found in nature, *i.e.*, the chemical composition of the materials composing the crust of the globe, is dealt with in works on Mineralogy.

       * Non-metals.   † Metals.

CHAPTER V

CHEMICAL EQUIVALENCE—ELECTRO-CHEMICAL
EQUIVALENCE—MULTIPLE AND RECIPRO-
CAL EQUIVALENCE—THE ATOMIC THEORY

Chemical Equivalence.—From the principles
of the definiteness of chemical change (p. 69)
and the Conservation of Mass (p. 76), it is
but a short step to the principle of chemical
equivalence. As with all broad scientific
generalizations, the conception which the
reader is now asked to grasp is simple enough
as an abstract notion, although some difficulty
may at first be experienced in mastering it.
It is, perhaps, needless to repeat that by
laboratory work the principle has been
deduced, and by quantitative manipulation
only can its significance be fully realized.
It is instructive as a chapter in the history of
Chemistry to read how nearly some of the
earlier investigators approached without actu-
ally reaching the principle of equivalence.
The historical treatment, however, cannot be
attempted here—it must suffice to ascertain

the meaning of the term as used now, without going over the steps by which the present position has been reached. Sufficient material in the way of facts and illustrations has been given to enable the subject to be dealt with in a general way.

In the first place, it must be noted that the terms " equivalence " or " equivalent " are expressive of facts only, and are independent of any theory or explanation. The facts in this case are those ascertained experimentally and enunciated in the previous chapters—the idiosyncrasies of the chemical elements, by virtue of which each element has its own special faculty of entering into partnership with other elements only in certain fixed proportions by weight. Out of these facts, there has, however, been developed one of the most illuminating theories that has been introduced into our science, so that the importance of equivalence has always to be realized by the student at a very early stage. In approaching this subject, it must be pointed out that we are not dealing with the likes and dislikes of the elements —why the elements show preferences such, for example, as that of iron for oxygen while this same metal refuses to combine under similar conditions with nitrogen (p. 37). In

considering the principle of equivalence we have nothing to do with the question why in particular cases chemical union is possible or impossible, but only with the quantitative relationship between what we may call the contracting parties, *i.e.*, the elements and compounds which can and do enter into combination directly, or which can be made to combine by indirect methods.

From the facts that combination does take place in fixed proportions by weight, and that the product of chemical union is homogeneous (Chap. II.), it follows that any such product, or, in other words, any particular chemical compound, however and whenever produced, always consists of the same elements combined in the same proportions by weight. This appears almost a truism now, because it is obvious that, if there were any latitude or variability in the ratio in which two or more elements combined to form a compound, there would be no homogeneity—we should have a mixture of two or more compounds. The principle is generally formulated as the law of *Constancy of Composition ;* and although it may appear obvious now, it was at one time the subject of much controversy, and this chapter of history is well worthy of consideration as an illustration of the method by which

truth is wrung from Nature by rigid experiment and logical reasoning. From the point of view of this law, it will be recognized that a chemical compound may be looked upon as being as true and as definite an individual form of matter as a chemical element. And it will be further realized that, as the complexity of chemical compounds increases, it may become more and more difficult to prove the individuality in particular cases. But the law is not thereby violated—there may be *apparent* indefiniteness, but this is the result of the imperfection of our practical methods, and the modern chemist still has faith in the principle.

For the elucidation of the principle of equivalence, a few simple cases may be considered. Oxygen and the halogens all form compounds with hydrogen, directly or indirectly. Oxygen and hydrogen explode when ignited to form water; fluorine and hydrogen explode spontaneously when mixed; chlorine and hydrogen explode when heated, or on exposure to bright light; and bromine and iodine can also be combined with hydrogen directly or indirectly. We are not now concerned with methods, but with products. The proportions by weight of the elements contained in these compounds are known

with great accuracy, both from analytical and synthetical evidence. In round numbers, and referring all the weights to the standard of one part of hydrogen, water contains 8 parts of oxygen, hydrogen fluoride 19 parts of fluorine, hydrogen chloride 35·2 parts of chlorine, hydrogen bromide 79·4 parts of bromine, and hydrogen iodide 126 parts of iodine. All these different weights of the respective elements, therefore, satisfy the same weight of hydrogen—they are equivalent, or equal in value, from the point of view of combining with a unit weight of hydrogen. Or take the case of those metals which decompose water (p. 83). If this process is followed quantitatively, it is found that, for every unit weight of hydrogen liberated, there are used up 12·2 parts of magnesium, 21 parts of iron, 23 parts of sodium, and 32·7 parts of zinc. Here, again, there is equivalence— these various weights represent quantities of different elementary substances which are of the same chemical value as measured by their capacity for displacing the same weight of hydrogen. Moreover, since this same weight of hydrogen is equivalent to 8 parts of oxygen, these equivalent weights of the metals are also equivalent to 8 parts of oxygen. And, since the compounds formed

by the action of water upon these metals under the conditions specified are oxides, or, as in the case of sodium, may be looked upon as arising from the combination of the oxide with water, it follows that the ratio between the weights of the metal and oxygen can also be expressed numerically on the oxygen scale :—Magnesium oxide, $12 \cdot 2 : 8$; iron oxide (" scale "), $21 : 8$; sodium oxide, $23 : 8$; zinc oxide, $32 \cdot 7 : 8$. And so, by ascertaining the proportion of metal to oxygen in other oxides, the equivalents of other metals with reference to oxygen and (by implication) to hydrogen could be found.

The doctrine of equivalence is, therefore, nothing more than the numerical expression of the definiteness of chemical change (Chap. III.). Perhaps it would be more correct, if we were dealing with the subject in historical sequence, to say that the definiteness of chemical change is the expression of the principle of equivalence, since the definiteness was established by quantitative studies of the kind illustrated above. But the order of statement is immaterial so long as the principle is understood. The " equivalent " is, thus, in abstract terms, a number expressing the parts by weight in which an element combines with or displaces some other element ; and

since hydrogen has the lowest equivalent, it will be convenient at this stage to refer these weights to the hydrogen standard. It is obvious that the conception as thus formulated is an idealized one, because there are many elements which neither combine with nor displace hydrogen; so that in such cases the equivalent can only be determined indirectly by reference to some other element of known equivalence. It will be shown, also, that the conception is not restricted to elements : since compounds are formed by the combination of elements in equivalent weights, it follows that if compounds combine among themselves—such, for example, as acid oxides and basic oxides (p. 108)—there must also be equivalence in such cases.

Electro-chemical Equivalence.—An electric current from a chemical point of view, and not regarded simply as a stream of electricity flowing through a metallic conductor, is a decomposing agent (p. 109). In accordance with the doctrine of the Conservation of Energy, a given quantity of electricity has its equivalent in terms of chemical work. In the case of electrolysis, the actual weights of elements liberated in a given time by a measured quantity of electricity measure the

chemical work done, so that the determination of the weight of, let us say, a metal deposited electrolytically in a given time is also a measure of the electrical energy used up. This is of importance in Physics as furnishing a chemical method for the measurement of electric quantity ; and the electro-chemical equivalents of some of the metals such, *e.g.*, as silver and copper, have from this point of view been determined with extreme accuracy. But the absolute weight of an element liberated in a given time by a measured current acquires also a chemical significance when we pass from the absolute to the relative—when the relative quantities of different elements liberated in the same time by the same current are considered. It is immaterial in this case how the electricity is made to do its work ; the current may decompose a salt, or an acid, or a base in solution or in the dry fused state (p. 109). Fused common salt, for example, yields 23 parts of sodium and 35·2 parts of chlorine ; a solution in water of hydrogen chloride gives for 1 part of hydrogen 35·2 parts of chlorine ; water, made to yield hydrogen and oxygen indirectly by an electrolysable acid in solution (p. 109), gives in round numbers 8 parts of oxygen for 1 part of hydrogen ; the volume ratio—2 of hydrogen : 1 of

oxygen—is revealed electrolytically, as it is
proved by chemical synthesis (p. 88). It is
unnecessary to multiply examples at this stage.
The point of supreme importance brought out
is that these relative weights of electrically
liberated elements are identical with the
chemical equivalents, a discovery due to
Faraday (1833). The establishment of this
law has led to some of the most fundamental
modern developments both of Physics and of
Chemistry; but its adequate discussion cannot
be attempted within the limits of this work.
Our consideration must be restricted to its
chemical significance in the narrow sense.

Multiple and Reciprocal Equivalence.—The
notion of equivalence would be a very
simple one if it could be stated in general
terms that the numbers representing the
equivalents of, let us say, the elements
A, B, C, D were always representative of
reciprocal equivalence—that whenever any
pair of these elements combined to form a
binary compound (*i.e.*, a compound containing
two elements) the latter could always be
formulated as AB, AC, AD, BC, BD, CD, etc.,
in which the juxtaposition of letters may
be taken as indicating chemical combination,
and the letters as representing equivalent
weights. But this statement would be too

sweeping—it is not generally true, but only partially true. The principle of reciprocity holds good for the simple cases referred to in the preceding sections ; but, when the whole of the facts are taken into consideration, complications arise owing to the circumstance that many elements can combine with each other in more than one proportion, each compound so formed being a perfectly definite chemical individual. One example of this has already been adduced in the case of iron, which can form three different oxides (p. 71). In all three oxides, the equivalent may be considered to be the weight of iron which combines with one equivalent, *i.e.*, 8 parts of oxygen. On this standard, the equivalent of iron in " scale " is 21 ; in rust (which contains 70 per cent. of iron, and therefore 30 per cent. of oxygen), the equivalent of iron is $18\frac{2}{3}$; and in the other oxide, which contains 77·8 per cent. of iron and 22·2 per cent. of oxygen, iron has the equivalent 28. Iron, therefore, in relation to oxygen has not one equivalent, but three equivalents.

Any number of cases could be adduced ; and, since the principle of multiple equivalence is of fundamental importance, a few other examples may be given. Twenty-three parts of sodium displace 1 part of hydrogen from

water, and combine with 8 parts of oxygen
(p. 110). The equivalent of sodium with refer-
ence to oxygen ($= 8$) is in this case 23. But
when sodium is heated to about 300° in pure
dry air, it forms another oxide in which $11\frac{1}{2}$
parts of sodium are combined with 8 parts
of oxygen. This element has, therefore,
with reference to oxygen two equivalents,
$11\frac{1}{2}$ or 23. The oxide of copper formed when
copper is heated in oxygen (p. 84) contains
$31\frac{1}{2}$ parts of copper to 8 of oxygen. By
chemical methods it is possible to prepare
another oxide which contains 63 parts of
copper to 8 of oxygen ; so that the equivalent
of copper may be $31\frac{1}{2}$ or 63. Carbon burns in
oxygen to form that dioxide which was
referred to as a constituent of the atmosphere
(p. 36); this gaseous compound of carbon
contains 3 parts of carbon and 8 parts of
oxygen. When carbon dioxide is heated in
contact with more carbon, another (gaseous)
oxide is formed which contains 6 parts of
carbon to 8 of oxygen. Moreover, when
carbon is intensely heated by an electric arc
in an atmosphere of hydrogen, it combines
with that element to form a gas—a compound
of carbon and hydrogen, and therefore called
a hydrocarbon—which is known as acetylene.
In this gas 1 part of hydrogen is combined

with **12** parts of carbon, so that this last element has the three equivalents, **3**, **6**, and **12**.

It is clear, therefore, that the conception of equivalence is not so simple as might be imagined on first approaching the subject. The numbers representing the equivalents are not absolute, but relative; an element A may have towards some other element B a perfectly fixed equivalent, but towards another element C, it may have the same equivalent that it has with reference to B and likewise another or other equivalents. A may have, also, a certain equivalent with reference to B or C under one set of conditions of combination, and other equivalents under other conditions of combination. All this has been established by quantitative analysis and synthesis—by determining with the greatest possible accuracy the relative weights of the component elements contained in chemical compounds, or the relative weights of the elements which enter into combination in synthetical operations. That these numerical results are expressive of some underlying physical reality is shown, also, by the coincidence of the chemical equivalents with the electro-chemical equivalents; because when an element has two equivalents, *i.e.*, forms

two distinct compounds with another element, it has been proved to possess two electro-chemical equivalents in all those cases where the two electrolysable compounds could be practically dealt with.

But, although the conception of equivalence is complicated by the multiple equivalence of many of the elements, a glance at the numbers given in the preceding examples will show that there is simplicity in the apparent complexity. Thus, the equivalent of carbon is 3, 6, or 12 ; of copper $31\frac{1}{2}$ or 63 ; of sodium $11\frac{1}{2}$ or 23, and so forth. These numbers stand in the relationship of simple multiples, so that the notion of equivalence must be widened by making allowance for the ratios of the combining weights being not only A : B, but also some simple multiple of A or B, or of both, such as 2 A : B, A : 2 B, 2 A : 3 B and so forth. This is what is known in Chemistry as the law of *Multiple Proportions ;* and in this sense only is reciprocity of equivalence or combining weight recognizable. Thus, the weights A and B which combine with a certain weight, C, of a third element need not necessarily be the same weights as those which exist in the compound AB, but may be some simple multiple such as 2 A with C, 3 B with C, etc.

One illustration should give a clear notion of this principle of *Reciprocal Equivalence*. In one of the oxides of iron, the equivalent weights are iron : oxygen $= 28 : 8$. In iron sulphide (p. 72), this same weight of iron is combined with 16 parts of sulphur. If there were general reciprocity of equivalence, it would be said, therefore, that 8 parts of oxygen should combine with 16 parts of sulphur ; but, in fact, this is not the case. Sulphur burns readily in oxygen to form an oxide—the so-called sulphurous acid gas, or sulphur dioxide—which is the oxide containing the smallest proportion of oxygen, viz., 8 parts of oxygen to 8 of sulphur. No lower oxide is known, so that 8 parts of oxygen and 16 of sulphur are not in this case equivalent ; in order to express the actual facts, we have to take two equivalents, *i.e.*, 8×2 parts of oxygen. Moreover, there is another oxide of sulphur in which 16 parts of sulphur are combined with 24 parts, *i.e.*, 8×3 parts of oxygen. The doctrine of equivalence is, therefore, only in harmony with the facts when sufficient elasticity is given to the conception to allow of the inclusion of cases of multiple equivalence and of multiple reciprocal equivalence ; and the main point brought out for assimilation

by the reader is the simple and integral character of the numbers expressing this multiplicity.

The Atomic Theory.—The doctrine of equivalence, even in its most elastic form, is still nothing more than a quantitative expression of the facts of chemical composition. Of course, there must be some underlying principle—some explanation of this simplicity of multiplicity. Such explanation was first definitely formulated in 1807-08 by John Dalton, who not only discovered the law of Multiple Proportions, but suggested a theory, the introduction of which marks one of the greatest epochs in the history of Chemistry. The reason why combination takes place in definite proportions by weight, and why, when the same element has more than one equivalent, the principle of integral multiples is maintained is, according to Dalton's explanation, because the combination is between the ultimate particles of which elementary matter is composed. This is the notion of the discontinuity or discreteness of matter referred to in a former chapter (p. 57), and now re-introduced in more exact terms. The " particles " of which matter is composed —whatever its state of aggregation—are, from Dalton's point of view, ultimate in the

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sense of being indivisible. For this reason he called them *atoms*.

The definiteness of combination by weight is attributable to the weights of the atoms—those elements of the elements. The atomic theory as thus introduced into Chemistry was the revival of very ancient views concerning the constitution of matter; but these older speculations had failed to influence the progress of science until given a definite quantitative meaning by Dalton. From the point of view of this theory, one atom having a certain weight can combine with another atom having also a certain weight, or one atom can combine with two, three, etc., other atoms; or again, two atoms can combine with three, three with four, and so forth. Any degree of complexity may exist; but, the atom being (by hypothesis) the ultimate unit, the passage from one compound AB to another containing the same elements in different proportions cannot take place but by whole multiples; fractional parts of A or B are inadmissible. It will be noted that at this stage the theory deals only with one fundamental attribute of matter, mass, as measured by weight. But, instead of dealing with this attribute in the gross as a general physical property of matter irrespec-

tive of individuality, the conception of the indivisible atom brings the sciences of Physics and Chemistry into an indissoluble partnership, for the atom of each element is, from this standpoint, a particle of matter which is indivisible, and which has a certain fixed weight, which weight is specific for each kind of atom, and is, therefore, a physico-chemical attribute.

The atomic theory as thus broadly outlined is, therefore, based entirely upon the observed facts respecting combination by weight. It postulates homogeneity among the atoms in the sense that the atoms of each element are assumed to be all alike—all cast in one mould, all possessed of the same weight, size, shape, and structure. That is why our imaginary being (p. 51), was supposed to be able to follow the movements of the different " particles " in a mixture of gases. Of course, the atoms must on this view have absolute weights, definite dimensions, shapes, etc. In its extreme form, the theory has been pushed so far as to claim that the atom is the ultimate component of the material universe—imperishable and eternal. The reader must, however, discriminate between ascertained concordance of facts with theory and speculative developments of theory,

however plausible in principle or stimulating in prompting further research. For the general purposes of chemical study, the atom may be regarded as indivisible. From the purely chemical point of view, the absolute weight is immaterial; it answers all practical purposes to deal with the weights, as did Dalton, as relative. By physical methods, it is possible to ascertain approximately the absolute weights and dimensions of atoms, but this part of the subject is beyond our scope; suffice it to say that the chemical atom is a particle of matter infinitesimally small—of a minuteness of size and weight which, even if expressed numerically, is beyond human conception.

The discussion of the truth of the atomic theory—whether the atom is a physical entity —belongs to the domain of Philosophy; we, as chemists, have only to deal with the doctrine in so far as it is in accordance with all the evidence which our science can produce, and with the verification of deductions drawn from it. It accounts for the definiteness of chemical combination by weight, and, as will appear later, it correlates and explains large bodies of facts which have been accumulated since its introduction by Dalton. It is the " head stone of the corner " in theoretical

Chemistry; and yet, as it stands, we all realize that it is incomplete—that vast developments may yet be looked for from both the physical and the chemical side. The mysteries of chemical change, the absolute transformation resulting from chemical combination, the likes and dislikes of the elements, their activities and inactivities, yet await explanation in terms of the atomic theory. The conception of the atom has simply shifted the responsibility of individual idiosyncrasies from matter in the gross to matter in detail —from the bulk to the ultimate particle.

The possibility of the atom being itself resolvable did not at first enter into consideration; it was assumed to be the final limit of the divisibility of matter. But the early crude notions concerning the nature of the atom have gradually undergone development, chiefly as the result of the study of the action of electricity upon matter in the gaseous state (p. 19) inaugurated in this country by Crookes and **J. J. Thomson.** Physical modes of dealing with matter undreamt of in the time of Dalton have led to the conclusion that the atom is not a structureless particle, but a complex, internally balanced mechanism, capable under certain conditions of being broken down into its smaller component

parts ; and it is accepted by many physicists and chemists as a plausible hypothesis that the atom is built up of particles of electricity (" electrons "). On this view, the conception of the material nature of the atom would have to be recast in terms of energy ; and it is for this reason that the possibility of matter coming into or going out of existence as the result of chemical change was considered worthy of being re-tested (p. 79). So far there is no direct evidence in support of this view —the most carefully conducted experiments have only served to confirm the doctrine of the Conservation of Mass.

The history of the development of the atomic theory will furnish fascinating reading for a future generation—experiments and hypotheses are now being pushed forward with a rapidity and with a boldness which entitle the chemist to say that the time is not yet ripe for attempting to complete the story. But it is along these lines—the study of the inner mechanism of the atom—that Physics and Chemistry are moving towards their point of convergence. No single attribute assigned to the atom during the early period of the theory has remained unchallenged. The idea of absolute uniformity of weight has been called in question ; and it has been

suggested that the property is an average one
—that there may be a certain range of varia-
tion in weight among the atoms of an element,
and that the apparent constancy in weight
is the statistical result of the practical
necessity of dealing with myriads in our
laboratory operations.   Of such variability,
however, we have at present no experimental
evidence.

Of the shapes and textures of the atoms we
know nothing with certainty.   The questions
whether they are hard and rigid, or elastic,
compressible, and deformable have been
discussed from time to time from the physical
side ; but no conclusion directly affecting the
chemical requirements of the theory has as
yet been arrived at.   The notion of an
imperishable atom has also been challenged,
first from the purely theoretical side regarding
the atom as a mechanism capable of reaching
a point of internal instability when a certain
degree of complexity has been attained, and
then from the observational side owing to
the discovery that one of the elements,
radium, is capable of giving rise to another
element, helium, by a process of spontane-
ous disintegration (Rutherford; Ramsay and
Soddy, 1903).   Here we are, therefore,
brought again directly into the domain of

Chemistry; and the alchemical dream of "transmutation" (p. 26) has, at least in this case, been realized. But the consideration of this subject belongs to a late chapter in the history of Chemistry, and the reader must accept this brief statement by way of preliminary introduction to the newly developed science of Radioactivity. (See, for instance, the volume on "Matter and Energy," by Mr. F. Soddy, in this Library.)

CHAPTER VI

SYMBOLS AND NOTATION—ATOMS AND MOLE-
CULES—ATOMIC AND MOLECULAR WEIGHTS
—THE DEFINITENESS OF CHEMICAL COM-
BINATION BY VOLUME—THE HYPOTHESIS
OF AVOGADRO

Symbols and Notation.—The transition from
the crude and primitive notions concerning
the chemical atom to the current conception
and use of the atomic theory represents a
period of more than a century. It was a
period teeming with interest from the histori-
cal point of view; but we must perforce pass
over the developmental phases and deal
with the science of Chemistry as it stands
to-day in the light of the theory. And,
before any substantial progress can be made,
it is necessary that the reader should master
at least the rudiments of chemical language—
they are simple, easy to understand, and
replete with meaning. Our alphabet is no
more than a set of shorthand symbols for the
atoms of the chemical elements. Symbols

137

in the form of letters of the alphabet have already been made use of in the last chapter in order to give general expression to the conception of equivalence; all that is now required of the reader is to attach a specific meaning to these symbols. The chemical symbol as at present used is the initial letter or letters in the name of the element, and this symbol stands for one atom of the element. There is no more mystery about this than in writing W. for Walter and Wm. for William; the only difference is that there may be multitudes of Williams and Walters, and that each individual is distinguished by the addition of one or more names. But we require no binomial system in Chemistry, because each symbol stands for one element only, and for one definite weight of that element —the weight of the atom with reference to some common standard.

The chemical elements have not been named on any coherent system; some of the names are survivals from a remote past, while those isolated in later times have received names indicating either some characteristic property, the natural source, or the country in which the isolation was effected. All that can be said is that the names of the more recently discovered metals have been given the

terminal syllable *um*. Each name (Latinized
in a majority of cases) is contracted into
an initial letter, or, if several elements
have the same initials, into two letters.   All
the elements named in the previous chapters
could have been made to tell their story more
concisely if symbols had been used.   A few
examples will serve to illustrate the use of
the chemical alphabet.   Thus **H, O, N, F,
I** stand respectively for one atom of the
non-metals hydrogen, oxygen, nitrogen, fluor-
ine, and iodine.   We cannot use C for chlorine,
because there are several other elements
beginning with C, so we write Cl for chlorine,
C for carbon, Cu for copper (*cuprum*), Ca
for calcium, and so forth.   We use Br for
bromine because B stands for boron; Bi for
bismuth, and Ba for barium.   S stands for
sulphur, Si for silicon, and Se for selenium.
Iron is Fe (*ferrum*), mercury or quicksilver
is Hg (*hydrargyrum*), silver is Ag (*argentum*),
gold is Au (*aurum*), sodium is Na (*natrium*),
and so forth.   The association of the symbol
with the name of the element is only a matter
of practice, and no great strain of memory
is required.   A complete list is given for
reference at the end of this volume.

Having mastered the alphabet, however,
the next step is to learn how to use it—how

to read a chemical formula. Here, again, the principle has already been made use of in order to illustrate equivalence; the only difficulty that the uninitiated reader is likely to meet is the confusion arising from the mixing up of chemical symbols with algebraical expressions, because, in chemical notation, the symbols are used in a different way. Thus, in algebra AB means $A \times B$, but the chemical formula AB stands for a chemical compound in which one atom of A is combined with one atom of B, each atom having its specific weight. So ABC in Chemistry stands for a compound containing one atom of each of the elements A, B, and C, and not, as in algebra, for $A \times B \times C$. In algebra the numerical coefficient multiplies any literal symbols that follow; thus $2A = 2 \times A$; $2AB = 2 \times A \times B$. In Chemistry the number of atoms is multiplied in the same way, so that 2A means two atoms of A; but in the case of compounds the whole weight of the compound is multiplied by the numerical coefficient. Thus, 2AB in chemical language means twice as much of the compound as is represented by AB, 3AB three times as much, and so forth. It is as though we wrote the equation $2AB = 2(A + B)$ in which the $+$ sign is made to stand for chemical combination. The

number of individual atoms in compounds is indicated by a small number placed *below* the symbol, to avoid confusion with the algebraical system of indicating the " power " by a small number placed above the symbol. Thus A^2B^3 means $A \times A \times B \times B \times B$; A_2B_3 means a compound containing two atoms of A *combined* with three atoms of B. A general chemical formula for a compound containing three elements would be $A_xB_yC_z$; and the multiplication of the whole weight represented by this formula would be $2A_xB_yC_z$, or $3A_xB_yC_z$, or $n A_xB_yC_z$.

Atoms and Molecules.—The congeries of atoms which elements form when they combine with themselves or with the atoms of other elements are termed *molecules*. This is a point of fundamental importance in modern chemical language, because it is impossible on this system to have an *atom* of a compound, although we might conceive the existence of an atom of an element. The justification for this distinction will be given immediately ; but we are now concerned only with notation, and it will be sufficient to point out to the student of the history of Chemistry that immense confusion was caused in the early period of the atomic theory through the failure to recognize that atoms and molecules

were different things. The atom is the smallest weight of an element that enters into the composition of the molecule of a compound, so that while $A + B$ stands for one atom of A mixed (not combined) with one atom of B, AB stands for one molecule of the resulting compound, 2 AB for two molecules, and so forth. And, since an atom can com bine with one or more similar atoms to form a molecule of the element, A_2 stands for one diatomic molecule of A, A_3 for one triatomic molecule ; and $2A_2$, $3A_2$, $2A_3$, etc., stand in these cases for two, three, and two of the molecules represented by A_2 and A_3 respectively. Moreover, the molecule of a compound may in some cases combine with one or more similar molecules to form compounds of double, treble, etc., molecular weight ; and this state of affairs is conveniently represented by such formulæ as $(AB)_2$, $(AB)_3$, etc., which therefore have a meaning different from that expressed by 2AB and 3AB, which indicate two and three distinct molecules of AB, whereas $(AB)_2$, $(AB)_3$, mean A_2B_2, A_3B_3, *i.e.*, one molecule in each case.

It may be of interest to point out that the introduction of the atomic theory and the clear recognition of the distinction between atoms and molecules has done more than any

other conception to bring the kindred sciences
of Chemistry and Physics into intimate associa-
tion.   In the direction of both the higher and
the lower limits of divisibility of matter, the
chemist and the physicist join hands, since
physical properties are associated with mole-
cular constitution and chemical properties
with the chemical atom ; while the newer
researches into the constitution of the atom
are laying a yet deeper foundation for both
sciences.

Atomic and Molecular Weights.—Since a
molecule is composed of atoms, its weight
as a concrete particle referred to the same
standard as that to which are referred the
weights of the atoms must be the sum of the
weights of the atoms of which it is composed.
But, in view of the principle of multiple
equivalence, it is evident that the determina-
tion, either by analysis or synthesis, of the
relative proportions by weight of the elements
contained in a compound does not decide the
question of the actual weight either of the
atoms or of the molecule.   Let us consider
one of the previous cases.   One part of hydro-
gen combines with 8 parts of oxygen to form
9 parts of water.   The simplest representa-
tion of this fact is the symbol HO, which now
stands for a molecule of water with a molecular

weight of 9 referred to hydrogen. Since 23 parts of sodium displace and are therefore equivalent to 1 part of hydrogen (p. 124), the corresponding oxide would be NaO with the molecular weight $23 + 8 = 31$. In sodium peroxide, $11\frac{1}{2}$ parts of sodium are combined with 8 parts of oxygen (p. 125)—what then is the atomic weight of sodium, $11\frac{1}{2}$ or 23 ? If $11\frac{1}{2}$, then the formula for the first oxide must be $Na_2O = (11\frac{1}{2} \times 2) + 8 = 31$, and of the peroxide $NaO = 11\frac{1}{2} + 8 = 19\frac{1}{2}$ to meet the arithmetical requirements. But $11\frac{1}{2}$ cannot be taken as the atomic weight of sodium in view of the fact that twice that weight is the smallest quantity which is equivalent to the standard unit of hydrogen. If we take 23 as the atomic weight, then the formula of the peroxide becomes $NaO_2 = 23 + (8 \times 2)$, and the molecular weight 39. And so, on the 23-sodium scale, the lowest admissible atomic weight for sodium, we have the two oxides NaO and NaO_2, with the atomic weight of oxygen taken as 8. But this view of the composition of the oxides introduces another equivalent for oxygen, viz., 16, since the equivalents are respectively $23 : 8$ and $23 : 16$; and the question now assumes the form—which, if either, is the atomic weight of oxygen ? If 8, then the formula of water is

as stated above, $HO = 9$; if 16, the formula must be $H_2O = 18$. On this same scale, the oxides of sodium obviously become Na_2O and Na_2O_2 respectively.

This last alternative now raises another point. In the peroxide, the ratio $Na : O$ is $23 \times 2 : 16 \times 2$, i.e., $46 : 32$; and this can, of course, be halved while still maintaining the atomic weight of 16 for oxygen. The formula then becomes NaO. Moreover, with the same atomic weight for oxygen, the formula of water might be H_2O, H_4O_2, or, generally $H_{2n}O_n$ without upsetting the ratio or violating the fundamental canon of an indivisible atom. It is clear, therefore, that the equivalent may or may not represent the weight of the atom; and it is equally plain that the answer to the questions :—which of the equivalents is to be taken as the weight of the atom ?—how many atoms are there in the molecule ? cannot possibly be given without further independent evidence.

It will be seen that the last question could be answered so far as concerns the hydrogen if it were possible to ascertain the relative weight of the molecule of water, because we should then know whether it was 9, 18, or 9n times as heavy as an atom of hydrogen. We might thus find out how many atoms of hydrogen

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the molecule actually contained, because, the ratio being always 1 : 8, a molecular weight of 9 would indicate that it contained one atom of hydrogen, a molecular weight of 18 that it contained two atoms of hydrogen, and so forth. But the question of the number of oxygen atoms in the molecule is still left open, even when the number of hydrogen atoms has been found, because, supposing we had found the molecular weight to be 18 and the number of hydrogen atoms 2, the molecular formula might be H_2O with one atom of oxygen of atomic weight 16, or H_2O_2 with two atoms of oxygen of atomic weight 8. Here, again, further information is required before it can be definitely decided whether the molecule of water contains 3 or 4 atoms. In the early days of the atomic theory, no such information was obtainable—or, to state the case accurately, such information was available, but it had not been utilized ; the far-reaching consequences of the study of chemical combination between elements and compounds in the gaseous state had not been fully realized. As a result of this lack of evidence, equivalent weights were often taken for atomic weights ; no direct method for the determination of the value of n in the equation $n \times equivalent = atomic\ weight$ had been

found. Methods of determining molecular weights had not been applied in Dalton's time—the distinction between atoms and molecules had not been clearly appreciated.

The Definiteness of Chemical Combination by Volume.—With the exception of the relations between the weights and volumes of hydrogen and oxygen in water (p. 88), chemical combination by weight has alone been considered up to this stage.   Now, the additional evidence required in order to decide definitely the relative weight of the atom of an element, when the relative weight of the molecule of a compound containing that element has been ascertained, is supplied, as hinted above, by the study of chemical combination by volume.   This presupposes that we are dealing with elements or compounds which are or can be made gaseous—it is bulk as distinguished from mass that has now to be dealt with.   But, before this part of the subject can be considered, the reader must be reminded of certain elementary physical principles.   All gases expand when heated, or when the pressure upon them is reduced ; they contract when cooled, or when the pressure is increased.   This is common knowledge ; but it can be stated in more precise terms.   The actual change in volume which takes place on

heating or cooling is $\frac{1}{273}$ per degree Centigrade
—a given volume of gas measured at 0° and the
pressure remaining constant, increasing by this
fraction of its bulk on being heated, and
diminishing to the same extent on being cooled
through 1°C.   So that at $-273°$, *i.e.*, 273° below
the freezing-point of water, the gaseous state is
presumably non-existent. That point is known
as the *absolute zero*; it is a mathematical abs-
traction, and has never yet been reached, but
recent researches on the liquefaction of the gases
by Dewar and Onnes have brought us within
three or four degrees of it.   The measurement
of the coefficient of expansion of gases is due
to Charles and Gay-Lussac, and the " law "
thus discovered is generally associated with
the name of Charles.

The effect of pressure upon gases is expressed
quantitatively by the statement that the
volume of a gas, the temperature remaining
constant, varies inversely as the pressure.
This means that, if the pressure is doubled,
the volume is halved; if the pressure is
halved, the volume is doubled, and so forth.
In mathematical terms :—Pressure × Volume
= Constant. This is known as the law of
Boyle (1626-1691).

Neither the law of Charles nor the law of
Boyle is obeyed absolutely by all gases;

there are departures depending primarily upon chemical idiosyncrasies—upon the specific nature of the element or compound. There are gases which approach perfection, and there are others which are imperfect gases. The laws in their most generalized form are physical, but in their detailed application they are equally chemical. For the present purpose, however, it is sufficient to regard them as purely physical. It is evident that in dealing with matter so sensitive as are gases to the influences of temperature and pressure, the conditions must be specified ; no comparison can be made between volumes of gases unless the conditions are comparable. Theoretically, any selected temperature and pressure might be adopted ; but practically it is convenient to suppose that the volumes are measured at 0°C, and at the average atmospheric pressure of 760 mm. of mercury. Of course, the measurements need not be, and in fact very seldom are, made at this temperature and pressure ; in practice the volume is measured, and the temperature and the pressure (as indicated by the barometer column) recorded. Then, by the laws of Charles and Boyle, the volume is reduced by calculation to the volume which the gas would occupy at 0°C. and 760 mm. ; the

so-called normal temperature and pressure. Of course, the method is imperfect ; it ignores the idiosyncrasies of the gases ; but, for practical purposes in comparing one gas with another, the errors thus included in the calculation are too small to seriously affect the result. The reader will now understand why in comparing gases it is a *sine qua non* that the conditions should be comparable.

Now, when chemical combination takes place between gases, it is found that there is as much definiteness about the process as there is about combination by weight. The ratios between the combining volumes are as fixed as are the combining weights ; and the numbers expressing these ratios are always simple, such as $1:1$, $1:2$, $1:3$, etc. And the same numerical simplicity is observed when the volume of the product is compared with the volumes of the components. Thus, there may be combination between equal volumes giving two volumes of the product : $1 + 1 = 2$. But the rules of arithmetic are not always obeyed ; one volume may combine with two, giving rise to two volumes of product, or one volume may combine with three, giving rise to two volumes of product. In these last cases, there is, of course, shrinkage or contraction. But it will be noticed

that, here also, the numerical relationships are simple. All that need be considered is the ratio between the volume of the mixed gases before and that of the product after combination. The results then come out in this way: $(1 + 1 =)2 : 2$; $(2 + 1 =)3 : 2$; $(3 + 1 =)4 : 2$, etc., so that in the first case there would be no contraction after combination; in the second case there would be contraction to the extent of $\frac{1}{3}$ of the volume of the mixed gases, and in the third case contraction to the extent of $\frac{1}{2}$.

These are observed facts—they were worked out with the greatest skill by Gay-Lussac (1778-1850), and the law of definite volume combination is associated with his name. A few examples will give greater precision to the conception of the principle. The halogens combine with hydrogen (p. 102). If the volumes of the elements are measured before, and of the products after combination—*all under comparable conditions*—it is found that equal volumes, say of hydrogen and chlorine, combine to give two volumes of hydrogen chloride, $1 + 1 = 2$; there is no contraction. Hydrogen and oxygen are contained in water in the proportion of two volumes of the former to one of oxygen (p. 88). If the water resulting from the combination of

measured volumes of hydrogen and oxygen is measured in the form of steam at 100° (because water is solid at 0° and 760 mm.) and compared with the volume of its components under similar conditions, it is found that it occupies the same space as the two volumes of hydrogen. So that in this case three volumes shrink to two—a contraction of one third.

In many cases, although compounds containing certain elements are well known and perfectly definite, yet it is difficult or even impossible to form such compounds by direct combination. For example, nitrogen forms with hydrogen a compound which is the familiar substance, ammonia, contained in "smelling salts"—a pungent smelling, strongly basic compound, gaseous at ordinary temperatures, liquid below − 34° and solid at − 77°. It is possible but not easy to bring about direct combination between nitrogen and hydrogen in such a way as to measure the volume relationships. In this case, which is typical of many others, it is much easier to decompose a measured volume of ammonia gas, say by a stream of electric sparks, and to measure the resulting elements. This is the analytical as distinguished from the synthetical method. It is thus found that from one volume of

ammonia there are produced two volumes of
a mixture of nitrogen and hydrogen—the
volume is doubled; and it is therefore con-
cluded that when nitrogen and hydrogen com-
bine there is contraction to the extent of one
half. And, since the mixed gases resulting
from the decomposition contain three volumes
of hydrogen to one of nitrogen, it follows
that the ratio of combining volumes is $3 : 1$,
and the ratio of the volume of the whole
mixture to that of the product $4 : 2$. Here
again the validity of the Gay-Lussac law
is noticed. Furthermore, the relative weights
of hydrogen and nitrogen in ammonia are
$3 : 14$, so that the equivalent of nitrogen in
this compound is $4\frac{2}{3}$, that being the weight
which combines with one part of hydrogen.

From the consideration of such cases there
arise almost spontaneously the questions:
—Is there any relationship between definite-
ness of combination by weight and by
volume? If such relationship exists, is it
explicable in terms of the atomic theory?
Does it enable us to state definitely how
many atoms of each element are present in
the molecule of a compound when the relative
weight of the latter is known?

The Hypothesis of Avogadro.—The answer
to all these questions can now be given. In

the first place, there is an obvious relationship between combination by weight and by volume. If, as stated above, one volume of chlorine combines with an equal volume of hydrogen, and if, as also stated (p. 119), the ratio of combination by weight is $1 : 35.2$, it follows that one volume of chlorine weighs 35.2 times as much as an equal volume of hydrogen. Again, in the case of water, two volumes of hydrogen combine with one volume of oxygen and the weights are $1 : 8$, so that 8 parts by weight of oxygen occupy half the space occupied by one part of hydrogen. For equal volumes, therefore, we have the relative weights $\frac{1}{2} : 8$, which means that oxygen, referred to hydrogen as unity, is 16 times heavier, bulk for bulk, under comparable conditions. And, yet again, in ammonia three volumes of hydrogen combine with one volume of nitrogen, and the relative weights are $1 : 4\frac{2}{3}$; from which it follows (since $4\frac{2}{3}$ parts of nitrogen occupy $\frac{1}{3}$ the space occupied by 1 part of hydrogen) that the relative weights of equal volumes are $\frac{1}{3} : 4\frac{2}{3}$, which means, when expressed in whole numbers, that nitrogen is, bulk for bulk, 14 times heavier than hydrogen. All this amounts, therefore, to the statement that the densities of the elements chlorine, oxygen and nitrogen are, on the

hydrogen scale, 35·2, 16 and 14 respectively. The relationship between weight and volume thus comes out in the form that the densities of the gaseous elements are equal to or are simple multiples of the equivalents :—chlorine, $35\cdot2 \times 1$; oxygen, 8×2; nitrogen, $4\frac{2}{3} \times 3$. These facts can, of course, be and have been ascertained experimentally, not only by determining the relative weights of the elements present in the respective compounds by analysis, but also by direct weighing of the gases under comparable conditions—*i.e.*, by determining their vapour densities.

Turning, in the next place, from the elements to the compounds resulting from their union, the densities can also be found from the quantitative composition and the volume occupied by the gas, or by direct weighing. Thus, 36·2 parts of hydrogen chloride resulting from the combination of 1 part of hydrogen with 35·2 parts of chlorine, occupy twice the volume of the hydrogen, as just explained. The density of hydrogen chloride is, therefore, $\frac{1}{2}$ of $36\cdot2 = 18\cdot1$. The 9 parts of water resulting from the combination of 1 part of hydrogen with 8 parts of oxygen occupy the same volume as the hydrogen, so that the density of water vapour is 9. The $5\frac{2}{3}$ parts of ammonia resulting from the combination of

1 part of hydrogen with $4\frac{2}{3}$ parts of nitrogen occupy $\frac{2}{3}$ of the volume of the hydrogen (because three volumes of hydrogen and one volume of nitrogen contract to two volumes of ammonia on combination), so that the ratio of the weights of equal volumes of hydrogen and ammonia is $\frac{2}{3} : 5\frac{2}{3} = 1 : 8\frac{1}{2}$; in other words, the density of ammonia on the hydrogen scale is $8\frac{1}{2}$.

Looking at these results in a broad way, it will be seen, in the first place, that we have really under consideration two distinct classes of particles or aggregates—elementary and compound. The former might be atoms or congeries of similar atoms; the latter must of necessity be molecules. It will be seen, also, that the densities of the elements bear some definite relationship to the weights of the atoms; but what that relationship really is could not be stated in numerical terms unless we knew the relative numbers of atoms in equal volumes. If it were assumed, for example, that these densities did actually represent the respective weights of the atoms, then we are confronted with the apparent paradox that the weight of the molecule of a compound is less than the sum of the atomic weights of its components. On the assumption that the *atoms* of chlorine, oxygen, and

nitrogen weigh 35·2, 16 and 14, the minimum weight of the *molecules* of hydrogen chloride, water vapour, and ammonia must be 36·2, 18 and 17 respectively. But the densities are 18·1, 9 and $8\frac{1}{2}$. The weight of water vapour contained in a volume which contains 1 part of hydrogen or 16 parts of oxygen is 9 ! Clearly 9 cannot be the weight of the molecule of water, or 16 cannot be the atomic weight of oxygen. The weight of ammonia which goes into the same space as 1 part of hydrogen or 14 parts of nitrogen is $8\frac{1}{2}$! The molecular weight of ammonia must be greater than $8\frac{1}{2}$, or the atomic weight of nitrogen must be less than 14. The weight of the whole cannot be less than the weight of its parts, unless matter is annihilated during chemical combination. The vapour densities of elements and compounds when compared do not decide the molecular weights of the latter any more than do the combining weights or equivalents of the elements contained in the compound unless there is made a certain assumption or hypothesis.

Such an assumption was made and enunciated as a hypothesis in 1811 by the Italian physicist Amadeo Avogadro. In the light of this hypothesis, all the above discrepancies disappear, and the vapour density of a com-

pound can be made to decide the weight of the molecule. According to Avogadro, equal volumes of all gases, elementary and compound, contain, under comparable conditions, the same number of molecules. It will be noted that the particles recognized by the hypothesis are molecules—not atoms; there is thus introduced the conception of the molecules of elements, as well as of compounds. This view of the constitution of gases harmonizes completely with those physical properties which find quantitative expression in the laws of Charles and of Boyle. But this side of the subject is dealt with in works on Physics under the kinetic theory of gases, and need not be enlarged upon here. Nearly half a century elapsed before the significance of the hypothesis in Chemistry was realized; it is mainly due to the advocacy of the late Prof. Cannizzaro in 1858 that it has become the foundation of modern chemical theory. Let us consider some of the previous examples in the light of Avogadro's conception.

One volume of hydrogen, which may be taken as the unit of comparison and assigned unit weight, combines with one volume of chlorine of weight 35·2 to form two volumes of hydrogen chloride of weight 36·2. The 35·2 parts of chlorine or the 1 part of hydrogen

occupy half the volume occupied by the product. Therefore the latter—the product volume—must, by hypothesis, contain twice as many molecules as there were of chlorine or of hydrogen in the original mixture. But the molecules of chlorine, although only half as numerous as the molecules of hydrogen chloride, have become equally distributed among the molecules of the compound, every one of which contains its full share of chlorine, *i.e.*, 35·2 parts by weight. Each molecule of chlorine has accordingly split into two equal parts—it is the molecule which has divided and not the atom, and the atoms are the components of the diatomic molecule, Cl_2, which is composed of two atoms of a weight 35·2 each. By precisely similar reasoning applied to the hydrogen molecule, we arrive at the conclusion that this also is a diatomic molecule, H_2, composed of two atoms of unit weight. Therefore, there is no violation of the atomic theory—the atom is still an indivisible particle; the combination between the elements is an interchange of partners, and not a simple juxtaposition of atoms.

From the same point of view, consider the case of water. The oxygen molecules must distribute themselves uniformly among double the number of water molecules, because the

water vapour occupies double the space occupied by the oxygen which enters into its composition. Here again, it is the molecule which divides, and the formula of the molecule must be O_2, irrespective of the question whether the atom weighs 8 or 16. So also with respect to ammonia, a given volume of nitrogen distributes itself uniformly throughout double the volume of ammonia, because one volume of nitrogen combines with three volumes of hydrogen to form two volumes of ammonia. This, in terms of the hypothesis, means that the nitrogen molecule is N_2, and that it divides into two equal parts when it combines with hydrogen.

Now sum up the facts and arguments setting out from the observation that the densities of the elements under consideration are $H = 1$, $Cl = 35 \cdot 2$, $O = 16$, $N = 14$:—

(*a*) 1 part by weight of hydrogen occupies half the volume of 36·2 parts of hydrogen chloride ; therefore 2 parts of hydrogen occupy the same volume as 36·2 parts of hydrogen chloride.

(*b*) 35·2 parts of chlorine occupy half the volume occupied by 36·2 parts of hydrogen chloride ; therefore 70·4 parts of chlorine occupy the same volume as 36·2 parts of hydrogen chloride.

(c) 16 parts of oxygen occupy half the volume occupied by 18 parts of water vapour; therefore 32 parts of oxygen occupy the same volume as 18 parts of water vapour.

(d) 14 parts of nitrogen occupy half the volume occupied by 17 parts of ammonia; therefore 28 parts of nitrogen occupy the same volume as 17 parts of ammonia.

To compare equal volumes of elements and compounds we have, therefore, to double the volumes and, by implication, the weights of the elements. Then we have a series of weights and volumes which are strictly comparable, the volumes all containing the same number of molecules. On this scale the hydrogen standard becomes 2, and the vapour densities of the other elements and of their compounds do represent the relative molecular weights. In other words, the volumes occupied by the molecular weights of elements and compounds are equal, and as this holds good for all elements and compounds (with certain exceptions which must be considered later) and irrespective of the number of atoms which form the compound molecule, we arrive at the generalized statement :—*Vapour density (referred to hydrogen as 1)* × 2 = *molecular weight*, or *molecular weight* ÷ 2 = *vapour density (referred to hydrogen as 1).* **And** so the

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question whether the relative weight of the molecule can be determined by ascertaining the vapour density is answered definitely in the affirmative. The apparent paradox previously raised—that the molecule of a compound can weigh less than the sum total of the atoms of its components—disappears when, as we now find, the molecular weight of hydrogen chloride becomes **36·2,** of water **18,** and of ammonia **17.**

CHAPTER VII

THE NUMBER OF ATOMS CONTAINED IN A MOLE-
CULE—DISSOCIATION AND ASSOCIATION—
AUXILIARY METHODS FOR DETERMINING
ATOMIC AND MOLECULAR WEIGHTS—THE
LAW OF DULONG AND PETIT—ATOMIC
AGGREGATES IN SOLUTION

The Number of Atoms Contained in a Molecule.
—The chemical molecule may be regarded in
the light of these conclusions as a weight of
matter representing in the case of compounds
an irreducible minimum, because any further
division must obviously lead to the removal
of atoms, *i.e.*, to decomposition, and the com-
pound, as such, ceases to exist. And, since
the weight of the molecule is the sum total of
the weights of its component atoms, we have
now to face the next question—whether, the
relative weight of the molecule being known,
it is possible to decide therefrom the numbers
of the atoms of the elements of which it is
composed. We know, for instance, that a
molecule of water has the relative weight 18,

163

and that it contains two atoms of hydrogen because it contains the divisible quantity of that element represented by H_2. The water molecule, therefore, contains $18 - 2 = 16$ parts of oxygen ; and the question is—how many atoms of oxygen does this represent ? Similar questions arise concerning all the compounds with which we have dealt.

It has already been pointed out that the formula H_2O_2, with an atomic weight of 8 for oxygen, satisfies the arithmetical requirements ; and it will now be seen that it also satisfies the molecular requirements, because the molecule of oxygen may be supposed to consist of 4 atoms, in which case its formula would be O_4, and the splitting of the oxygen molecule would be represented by the equation $O_4 = 2 O_2$ The answer to the question now raised is really in principle a very simple one. It is given by taking a consensus of evidence—by a kind of Referendum to all the known gasifiable compounds of the element in order to find out, by comparing the weights of the element contained in the molecules of the various compounds, the smallest weight contained therein. That weight is reasonably taken to be the irreducible minimum of the element, *i.e.*, its atomic weight. It corresponds with the definition of the atom

previously given (p. 142)—the smallest weight of the element which enters into the composition of the molecule, or which can be separated from the molecule by decomposition. In this way we find that the smallest weights of chlorine, oxygen, nitrogen, etc., contained in the molecules of any of their compounds are, respectively, 35·2, 16 and 14; and we take these as the weights of their atoms—we find the value of n in the equation $n \times equivalent = atomic\ weight$ (p. 146). In this case for Cl, $n = 1$; for O, $n = 2$; and for N, $n = 3$. And thus we are enabled to write the formulæ of the compounds HCl, H_2O and NH_3, and to indicate the actual numbers of atoms composing their molecules. Furthermore, we can represent the formation of these compounds from their elements by equations which are both chemically and arithmetically true :—

$$H_2 + Cl_2 = 2\ HCl\ ;\ 2\ H_2 + O_2 = 2\ H_2O\ ;$$
$$N_2 + 3\ H_2 = 2\ NH_3.$$
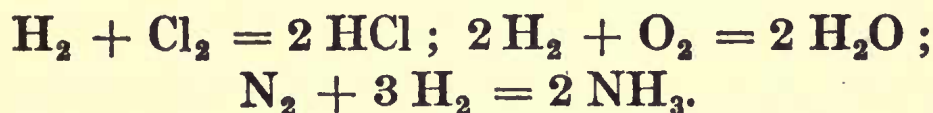
It has already been claimed that the symbolical language of Chemistry is full of meaning. The reader will now perceive the wealth of truth embodied in these symbols. The formula for a chemical compound, $A_xB_yC_z$, stands for one molecule—for a weight

of the compound made up of the sum of the weights of x atoms of A, y atoms of B, and z atoms of C. It represents also a weight of the compound which in the gaseous state—if it is gasifiable—occupies the same volume as the molecule of hydrogen, $i.e.$, H_2. It will be seen, also, that the symbols for the atoms of those elements which possess diatomic molecules represent half volumes; the atomic weights of H, Cl, O, N, etc., all occupy the same volume in the gaseous state. The law of definiteness of combination by volume (p. 147) is thus explained—the atomic weights must combine in equal volumes, or in some simple multiple of these volumes.

Dissociation and Association.—There are certain elements and compounds whose vapour densities are apparently unconformable; there are discrepancies between the numbers obtained for their atomic or molecular weights and the numbers deduced from the law of uniformity of atomic and molecular volumes. But this nonconformity is not paradoxical —on the contrary, it is instructive in the highest sense. From the story of such cases we get a glimpse into new principles. Let us consider some of the facts.

The atomic weight of sulphur as deduced from the analysis and vapour densities of its

gaseous compounds is 32.   If it were conformable, its molecular weight should, therefore, be 64, and its vapour density 32.   In fact, this element has two vapour densities, according to the temperature at which the vapour is weighed.   At its boiling-point under atmospheric pressure (448°), its vapour density is 128 ; and at 1700° its vapour density is normal, *i.e.*, 32.   Translate these facts into terms of the atomic-molecular theory, and consider their meaning.   At 448° the volume of sulphur vapour which occupies the space occupied by 1 part by weight of hydrogen weighs 128, and its molecular weight is accordingly 256.   Similarly, its molecular weight at 1700° is 64.   There is really no mystery about this.   If, as the evidence shows, the atom weighs 32, then at 448° the molecule must contain 8 atoms, *i.e.*, $32 \times 8 = 256$; the formula is S_8.   At 1700° the molecule must for the same reason be S_2 ; and, as the vapour cools down from 1700° to 448°, the simpler aggregate of 2 atoms condenses to the more complex aggregate of 8 atoms.   This brings out the principle of *Dissociation and Association*—terms which, in the light of the foregoing example, should be self-explanatory. Again, phosphorus—the highly combustible non-metallic element used in the manufacture

of lucifer matches—has an atomic weight of about 31, as determined by the usual methods. At 313° the vapour density gives a molecular weight of $31 \times 4 = 124$, and the molecule is P_4. As the temperature of the vapour is raised, the P_4 *dissociates*, and at 1700° it is largely resolved into P_2.

In a similar way, and by means of modern appliances which are described in works dealing with practical Chemistry, the molecular weights of many other elements reveal this principle of dissociation and association. Thus, iodine of atomic weight about 127 at 448° is normally I_2; at 1700° it completely dissociates into I—the molecule and the atom at this temperature are the same; *the molecule is monatomic.* Sodium, zinc, mercury, etc., have by a similar method been shown to exist at high temperatures as Na, Zn, Hg, *i.e.*, as monatomic molecules.

So also with regard to compounds. Hydrogen fluoride (p. 102) is chemically analogous to hydrogen chloride, the vapour density of which accords with the formula HCl. But the vapour density of the fluoride indicates that below 30° its molecule is $(HF)_2$, *i.e.*, H_2F_2, and that at 88° dissociation has taken place; as the temperature falls association takes place :—$2HF \rightleftarrows H_2F_2$. The reader will inci-

dentally notice the potency of our symbolical language. It is only necessary to call attention to a certain oxide of nitrogen, to the compound which phosphorus forms with chlorine (phosphorus pentachloride), or to the compound, ammonium chloride, formed by the direct union of one molecule of ammonia with one molecule of hydrogen chloride, as further illustrations of the principle and to write the story of their dissociation and association by means of such schemes as these : $N_2O_4 \rightleftharpoons 2NO_2$; $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; $NH_4Cl \rightleftharpoons NH_3 + HCl$.

The only information not included in the symbolical representation of the process is the temperature at which dissociation takes place in each case, and the influence of pressure upon the amount of dissociation. The combination between compound molecules, such as ammonia and hydrogen chloride, furnishes an illustration of the extended principle of equivalence (p. 121), since 17 parts of ammonia and 36·2 parts of hydrogen chloride represent equivalent weights of these two compounds.

Auxiliary Methods for determining Atomic and Molecular Weights.—The reader who has followed the development of the principles of chemical science up to this point will now

realize that the methods employed for the determination of the relative weights of atoms and molecules enable us to state definitely that, under such or such conditions, such or such atomic aggregates exist. All the gaseous elements referred to in former chapters form diatomic molecules. Our imaginary being of the second chapter who was capable of following the gyrations of the " particles " of air would, in fact, see vast crowds of twin pairs of atoms of nitrogen, smaller numbers of twin pairs of atoms of oxygen, and still smaller numbers of triatomic groups constituting the molecules of water (H_2O) and carbon dioxide (CO_2). And he would also see now and again solitary monatomic nomads of certain very rare gases (argon, neon, krypton, xenon), which have already been stated to have been detected in late years as constituents of the atmosphere. But, great as is the insight into the constitution of matter gained by this combination of chemical and physical methods of attacking the problem, it must be realized that the results are true only within the limiting conditions of the observations. The state of aggregation revealed is true within the ranges of temperature and pressure available for the determination of atomic and

molecular weights; but it must not be inferred that no further disaggregation is possible at extreme temperatures (say celestial), or under the influence of other disintegrating forces. Neither can it be asserted that in the other direction—in the passage from the gaseous to the liquid or solid state—there is no greater complexity than that indicated by the molecular formula as ascertained by the above methods.

Take the case of the elements. Under infinitesimal pressure, *i.e.*, in a vacuous space containing comparatively few molecules, there is physical evidence that the atoms are capable of being broken down by an electric discharge into smaller particles—" corpuscles," or " electrons," or whatever they may be (p. 134). But this ultra-dissociation by ultra-chemical means in no way conflicts with the views concerning the atom derived from the study of its chemical and physical attributes under ordinary conditions. It is supplementary information concerning the inner mechanism of the atom as a discrete particle of matter, of which the direct bearing upon the nature of chemical change has yet to be deciphered. The atom may be knocked to pieces by an electric discharge in a high vacuum, or may be disintegrated in the

atmosphere of the hottest stars (Lockyer);
but in the course of all the ordinary chemical
transformations which matter undergoes on
this earth it may still be regarded as the
indivisible particle.

So also in the other direction—in the way
of increased complexity—the molecule, let
us say, of vaporous water, H_2O, may not be
the molecule of liquid water, which is cer-
tainly $(H_2O)_n$. The value of n cannot be said
to have been definitely established yet. So
generally in the case of solids, we have no
criterion of the state of molecular aggregation
based on vapour density determinations only.
The three oxides of iron, for example (p. 124),
have the formulæ Fe_2O_3 (rust), Fe_3O_4 (scale),
and FeO respectively; the sulphide (p. 128) has
the formula FeS, and the iodide (p. 73) FeI_2.
But these are minimum formulæ—we cannot
convert any one of these compounds into
vapour; and the atomic weights of the
elements composing these molecules have
been determined independently of these
particular compounds. The molecules of the
solid compounds may be, and probably are,
multiples of these formulæ. Then, again, in
the case of the elements, the molecule of
the liquid or solid might be a multiplex aggre-
gate of gaseous molecules. Moreover, there

are many elements which, like carbon, for example, cannot be gasified at any manageable temperature; and there are elements which are not only non-volatile, but which form no gasifiable compounds. It is evident, therefore, that other evidence is wanted; the method based upon the hypothesis of Avogadro is inapplicable in such cases as those referred to above—auxiliary methods are needed.

The Law of Dulong and Petit.—The reader will learn from Physics that different kinds of matter require different quantities of heat to raise equal weights through the same range of temperature. This is, therefore, a specific property of matter; and the quantity of heat required to raise some particular substance through some definite range of temperature is said to be the *specific heat* of that substance. The standards in use are generally 1°C. and the specific heat of water as unity; the quantity of heat required to raise one gram of water through 1°C. is known as the *calorie.* We cannot deal here with the physics of this property of matter—why different substances should require different quantities of heat to produce the same visible effect upon a thermometer; neither is it necessary to describe the methods of deter-

mining specific heat, as these are dealt with in works on Physics. From the chemical point of view, this property of matter can be utilized as an auxiliary method for checking atomic weights. It was discovered by Dulong and Petit (1818) that if, instead of comparing the specific heats of equal weights of the chemical elements in the solid condition, the specific heats of weights of the elements proportional to their atomic weights are compared, then the fact is revealed that all the elements have the same *atomic heat*. In other words, the property in question is a property of the atom ; the atoms all require the same quantity of heat to raise them through the same range of temperature. The specific heats of the elements are thus inversely as the atomic weights, so that *Atomic Weight × Specific Heat = a Constant*. The value of that constant is between 6 and 7, and averages 6·4, so that **6·4** ÷ *Specific Heat = Atomic Weight*.

This law is only approximative, and there are deviations from it—some to a considerable extent. But these abnormalities arise from the circumstance that in the case of certain elements the specific heat only approaches the normal value at high temperatures. Passing over these exceptional cases, the remainder of the elements conform closely with the law.

But, although the latter is only approximative, it follows from the relationship between equivalents and atomic weights that there is a wide margin within which the numerical results may be allowed to fluctuate. The equivalents are exact—as accurate as can be determined by the most refined and delicate methods of analysis. But, after we have ascertained the equivalent, its relationship to the weight of the atom has, as already pointed out, to be settled by independent evidence. In cases where the molecular weight cannot be determined directly, or where the element forms no gasifiable compound, the specific heat gives valuable information. The whole point to be decided is the same as that which arises in the case of the gaseous elements, viz., whether the equivalent A represents the weight of the atom, or whether the atomic weight is 2A, 3A, etc. That is why this auxiliary method based on the law of Dulong and Petit admits of considerable numerical latitude. A few illustrations will enable the reader to appreciate its value :—

The vapour density of mercury on the hydrogen scale is 100, so that its molecular weight is 200. If the molecule consisted of two atoms, the atomic weight would be 100. But the specific heat of solid mercury is ·032

(water $= 1$) and $6 \cdot 4 \div \cdot 032 = 200$, and so the atomic weight of mercury is taken as 200, and that is one of the reasons why the molecule is considered to be monatomic (p. 168). Again, which of the equivalents of iron (p. 124) represents the weight of the atom? The specific heat of iron is $\cdot 112$, and $6 \cdot 4 \div \cdot 112 = 57 \cdot 1$. None of the three equivalents, 21, $18\frac{2}{3}$, or 28, represents the weight of the atom, but the nearest is evidently 28×2; and it is for this, among other reasons, that the atomic weight of iron is, in round numbers, accepted as 56. Copper forms two oxides, and has, therefore, the two equivalents $31 \cdot 5$ and 63 (p. 125). Which of these, if either, represents the weight of the atom? The specific heat of copper is $\cdot 994$, and $6 \cdot 4 \div \cdot 994 = 64 \cdot 4$. There is no doubt, therefore, in spite of the deviation, that the second of these equivalents represents the weight of the atom.

Atomic Aggregates in Solution.—The resources at the disposal of chemists for determining the molecular weights of compounds which cannot be gasified have been added to in recent years by the introduction of other auxiliary methods. These newer methods are based upon physical principles, which cannot be considered in detail here; but a general notion can be outlined. Let us begin

with some facts. Everybody is familiar with the fact that certain liquids, such as water, dissolve certain solids (p. 85), such as sugar or salt. Other liquids, such as alcohol (spirit of wine), will mix with, *i.e.*, dissolve in water in all proportions. So, also, gases dissolve in liquids like water, and such solutions give up the gas again when heated. This property of liquids may be looked upon as a physico-chemical property, because it is specific; solubility and insolubility, or the degree of solubility under given conditions, are properties dependent upon the nature of the solvent and solute. By " nature " in this case, chemical nature is meant. For the present purpose water may be taken as a typical solvent, and sugar as a typical solute.

This familiar substance is composed of the three elements, carbon, hydrogen, and oxygen, in the atomic proportions indicated by the formula $C_{12}H_{22}O_{11}$. This is the result of the analysis of sugar, which contains in 100 parts by weight 42·1 parts of carbon, 6·4 of hydrogen, and 51·5 of oxygen. The formula, as in all such cases, is simply the percentage composition translated into terms of atomic weights (in round numbers, $C = 12$; $H = 1$; $O = 16$). But this formula is a minimum formula; the sum total of the atomic weights

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will be found to be 342, which may or may
not be the molecular weight. The molecule
cannot weigh less than this, because if we
halve it we introduce the inadmissible formula,
$C_6H_{11}O_{5\frac{1}{2}}$, containing a half atom of oxygen.
Neither can it be decided whether the mole-
cular weight is a multiple of 342 by determin-
ing the vapour density, because sugar is
completely decomposed by heat. This illus-
trates a class of cases in which the newer
methods supply the required information.

The point on a thermometer scale at which
a liquid when cooled passes into the solid
state is said to be the freezing-point ; and the
point at which the liquid when heated passes
into vapour under any given pressure is the
boiling-point at that pressure. Thus, the
freezing-point of water is 0° (273° absolute),
and, under ordinary atmospheric pressure,
the boiling-point is 100° (373° absolute).
Now, it is a well known fact that a solution
freezes at a lower temperature, and boils at
a higher temperature, than the pure solvent.
The physical interpretation of this fact cannot
be discussed here ; the two properties referred
to are really different aspects of the same
physical principle, and so the freezing-point
only may be considered in order to simplify
matters.

It has been established by experiment (Raoult, 1883) that there is a definite relationship between the depression of freezing-point of a solution and the molecular weight of the solute. That relationship is broadly expressed by the statement that, for any particular solvent and with equal concentration (*i.e.*, percentage of solute in solvent), weights of different substances corresponding to the molecular weights produce the same amount of depression. It is not possible to enter further into details either of principle or of technique, but it will be seen in a general way that the introduction of this principle adds to the methods available for the determination of molecular weights. If the depression produced by any particular solvent with various solutes of known molecular weight (*i.e.*, determined by other methods) in known degrees of concentration is ascertained experimentally—and the more dilute the solution the more concordant the results—then the molecular weight of a substance of unknown molecular weight can be determined by a simple calculation when the depression of freezing-point produced by a known weight of the substance in a known weight of the solvent is ascertained by observation.

It must be understood that this method is

applicable only in cases where there is no chemical action between the solvent and solute. It must also be pointed out that the method is inapplicable to acids, bases, or salts—in other words, to electrolytes (p. 109)—because there is evidence that in the case of these compounds solution, at any rate in water, is accompanied by a resolution of the compound into component parts corresponding with those which travel to the respective poles during the process of electrolysis (p. 111). In such solutions there are, therefore, contained a larger number of component parts—known as *ions*—than is the case with unresolvable non-electrolytes, such as sugar; and the depression of freezing-point produced by compounds which undergo this *ionic dissociation* is, therefore, incomparable with that produced by compounds of the other type.

From the practical side, the reader must realize, also, that the depression which is measured in these cases is extremely small, and necessitates a refinement in thermometric methods quite beyond the ordinary experience of the casual observer. To give one illustration, it may be mentioned that a solution of one part of sugar in 100 parts of water produces a depression of ·058°, *i.e.*, the solution

solidifies at $-0.058°$ instead of at $0°$. The depressing value of water being known for many compounds of known molecular weight, it will be found on calculation that the depression produced by sugar corresponds most closely with the molecular weight 342, and that the formula $C_{12}H_{22}O_{11}$ is, therefore, the molecular formula. This means that the molecule of sugar contains $12 + 22 + 11 = 45$ atoms, and that its weight on the hydrogen scale is 342. The state of atomic aggregation in which sugar exists in solution is the same as that which it would possess in the state of vapour, were it possible to convert this compound into vapour without decomposing it.

The contemplation of such conclusions as have now been set forth—conclusions based upon experimental observations interpreted by hypothesis—will assuredly serve to justify the claim of Chemistry to take rank as a science which is penetrating more and more deeply into the inner mysteries of matter. The atoms and molecules which are dealt with by such methods as have been considered —methods which are by no means exhaustive of all our resources—are legitimately conceived as physical entities ; and every advance in our knowledge of the physical and chemical properties of matter has served to strengthen

the reality of this conception. Some further developments will be discussed as far as possible in the short space remaining at our disposal. It may be fairly asserted that the atoms and molecules which modern chemical philosophy has called into existence " out of the void and formless infinite " have become the common property of thinkers and workers in every department of science.

CHAPTER VIII

DETERMINATION OF THE RELATIVE WEIGHTS OF THE ATOMS—THE ISOLATION OF DEFINITE SUBSTANCES—CHEMISTRY AS AN EXACT SCIENCE—THE STANDARD OF ATOMIC WEIGHTS—CHEMICAL ARITHMETIC —VOLUMETRIC RELATIONSHIPS

Determination of the Relative Weights of Atoms.—The fundamental units of matter which have thus been made the basis of the modern interpretation of chemical phenomena exist in the 82 different modifications representing the known chemical elements. The varying characters of the individual elements are qualitative expressions of the idiosyncrasies of the atoms ; with the progress of discovery, we may hope to be able to express these differences more and more precisely in quantitative terms. It has been shown in the previous chapters that the main attribute of the atom which is at present dealt with quantitatively is the relative weight. The question now arises—how is this weight

ascertained ? The relative weight of an atom is a " Constant of Nature " in the same sense as, let us say, the length of an ethereal wave corresponding to a particular colour, or the number of vibrations corresponding to a particular musical note. It is evident, therefore, that a character of such fundamental importance as the atomic weight must be expressed numerically with the utmost obtainable accuracy.

In the foregoing chapters, certain atomic weights have already been assigned to some of the elements. The reader has been given to understand in a general way that these numbers are found by determining the relative quantities of the elements present in compounds, and then ascertaining the molecular weight of the compound by one or another of the available methods. It must be realized that the physical methods, such as vapour density determination, depression of freezing-point, raising of boiling-point, determination of specific heat, etc., are not methods of precision in the strict sense, but methods of control—they decide only the total number of atoms composing a molecule, and the particular equivalent or combining weight which represents the weight of the atom. If, therefore, these methods are methods of

control, what is it that they do control ?—
evidently the equivalents determined by
analysis or synthesis.

The determination of the atomic weight of
an element resolves itself into a question of
quantitative composition as ascertained with
all the precision attainable by human skill. It
is not a question as to whether the atomic
weight of oxygen is 8 or 16, of sulphur 16 or
32, of carbon 3 or 12, of nitrogen $4\frac{2}{3}$ or 14, of
iron 28 or 56, of mercury 100 or 200—these
broad issues may be taken as settled by the
methods of control. It is now a question of
accuracy in the decimal places, for these atoms
are the gifts of Chemistry to universal science,
and the account of their attributes must be
rendered with all the precision demanded by
the exact sciences.

It is beyond the scope of this work to
describe in detail the methods of determining
atomic weights. The chemical changes dealt
with are for the most part simple. For
example, direct combination between a metal
and a halogen when giving rise to a definite
weighable compound gives the ratio :—*Metal:
Halogen.* As an actual case, the determination
of the equivalent of silver with respect to
chlorine may be cited. A known weight of
silver converted into chloride by combination

with chlorine gives so much silver chloride. Using symbols, and expressing the change in the form of an equation, we have :—$2 Ag + Cl_2 = 2 Ag Cl$. The gain in weight represents the chlorine combined with the silver ; the ratio $Ag : Cl$ has been found. It will be noted incidentally that no molecular formula has been assigned to the silver, because the state of atomic aggregation of the solid metal is unknown (p. 172) : it may be Ag_x, the value of x being unknown.

Again, most of the elements can be made to combine either directly or indirectly with oxygen. When the oxide is a definite compound, the weight of oxide obtained from a known weight of the element gives the ratio : *Element : Oxygen.* Conversely, an oxide of definite composition when resolvable, say by heat, into element and oxygen, gives the same information. Many metallic oxides which do not part with their oxygen on heating alone are reduced to the metallic state when heated with some element which can combine with the oxygen. Carbon and hydrogen are such *reducing agents.* The oxides of iron, for example, can all be reduced to iron by strongly heating them with charcoal or some other form of carbon. That is why the metal iron was referred to as an artificial product

(p. 87), because the metal is obtained from its ores by such treatment. The oxides can also be reduced by heating them in an atmosphere of hydrogen, and this completes the proof that these oxides consist only of metal and oxygen (p. 71). The loss of weight thus undergone by the oxide on reduction by hydrogen might be made to give the ratio :—*Metal : Oxygen*. And, since in this case the oxygen of the oxide forms water with the hydrogen, the weight of water gives also the ratio $O : H$ in water. To take another example :—The oxide of copper formed when copper is heated in oxygen (p. 84) is a perfectly definite oxide, which is reduced to copper on heating with carbon or in hydrogen, the change, under the latter condition, being $CuO + H_2 = Cu + H_2O$. Here again it will be noted that no molecular formula is assigned to the oxide or to the metal, the reason being as above given—our ignorance of the molecular weights of solid elements and compounds. In this example, a known weight of oxide loses so much on reduction ; the loss represents oxygen. This known weight of oxygen gives so much water, the gain in weight being due to the hydrogen combined with that quantity of oxygen—the ratio $O : H$ in water has been determined.

There is no royal road to the determination

of atomic weights—every available method is utilized : it is entirely a question of practicability. Since, in the case of some of the elementary gases, the densities referred to hydrogen represent the atomic weights (p. 166), a direct determination of density gives the necessary information with a degree of precision limited only by the accuracy of the experimental methods. If a metal can be deposited in a weighable condition by the electrolytic decomposition of its salts, the electro-chemical equivalent (p. 121), gives the required information. It can be asserted as a general principle that for the determination of atomic weights the main requirement is purity—the materials used, elements and compounds, must be chemical individual substances in the strictest sense realizable.

The Isolation of Definite Substances.—The whole development of Chemistry is intimately bound up with the practical necessity of isolating the various forms of matter, elementary and compound, in such a state of purity that a chemical individual substance is obtained. The foundations of our science are based on the study of individual substances ; and the degree of exactness that has been reached is a measure of the success of our laboratory methods. The reader who ap-

proaches Chemistry from the purely literary side must thoroughly grasp this fundamental reality—he must realize to the full extent the significance of the statement that Chemistry is an art as well as a science (p. 31). In no branch of practical work is the standard of individuality, *i.e.*, of purity, of more vital importance than in the materials used for the determination of atomic weights. It is for this reason that the general question of the isolation of individual substances has been brought forward here. The discussion of practical methods is beyond the limits of this work; they cannot be mastered by simply reading about them, but only by that combination of manual skill, judgment, and resourcefulness which is essential for accuracy in this kind of work. The separation of individual substances—in other words, their purification, is effected by processes which are familiar enough as laboratory operations. If a substance has a definite boiling-point (p. 59), it can be distilled, and a fraction having a constant boiling-point isolated; if it can be vaporized by heat and condensed in the solid form, it can be purified by sublimation; if it separates from its solution in a crystalline form when the solvent is evaporated, the associated impurities can in this

way be removed by a sufficient number of crystallizations ; if the substance in solution can by interaction with some other substance be converted into an insoluble compound it can be purified by precipitation.

But, in spite of all our resources, an abso lutely pure substance is so extremely difficult to obtain that it may almost be regarded as a mathematical abstraction.   Matter pure enough to withstand chemical examination may still be shown by more delicate physical tests, such as by means of the spectroscope, to contain traces of foreign substances.   The atomic weights in use are necessarily of different degrees of exactness, and finality has not yet been reached—the work is still in progress, and accuracy is being pushed further along the line of decimal places.   The results obtained by different experimenters are considered by an International Commission, under whose auspices a list of atomic weights is published annually.   The list for 1912 is given at the end of this volume.

Chemistry as an Exact Science.—It is not claimed that Chemistry ranks with the exact sciences in the sense of having reached the purely deductive stage ; but in every direction in which quantitative treatment is possible the relative weights of the atoms come sooner

or later into consideration. Hence the necessity for accuracy in these constants, the responsibility for the determination of which is necessarily thrown ultimately upon the chemical balance. This instrument, compared with those used in some of the most delicate physical measurements, may perhaps be considered coarse. But, for all practical purposes, accuracy to the 1-10,000th of a gram, *i.e.*, 1-10th of a milligram, is sufficient; for the more refined work sensitiveness to 1-200th of a milligram is obtainable. The time may come when, for the investigation of the more recondite attributes of the atom, a higher degree of precision will be necessary; and it may be well to point out, therefore, that there has recently been added to the resources of the physicist and chemist a micro-balance constructed of quartz capable of weighing the almost inconceivably small quantity of 1-10,000th of a milligram.

But the difficulty now rests not so much with the instrument as with the matter; ultra refinement in weighing unless the substance is really " individual " is suggestive of " straining at a gnat and swallowing a camel." Some of the atomic weights are confessedly uncertain; on account of those difficulties of purification which have just been indicated,

it is recognized that in many cases revision is necessary. In no case, however, is the responsibility of fixing the atomic weight thrown upon the analysis or synthesis of one compound of an element when several compounds are available. The degree of precision reached is evidently dependent upon the number of independent sets of observations ; all those atomic weights which have been determined with the greatest accuracy are based upon converging lines of evidence. In modern times the science of Chemistry largely owes its advance towards exactness in this direction to the life-long labours of men like Stas, Morley, Richards and Clarke.

The Standard of Atomic Weights.—Although hydrogen, having the lowest atomic weight, was at first naturally taken as the standard, for practical purposes this element is by no means a convenient one. It is evident that any element of which the equivalent with respect to hydrogen has been determined with precision may be made the standard ; the translation to the hydrogen scale of the atomic weight determined with reference to such other element then becomes a matter of calculation. Hydrogen forms but few compounds with other elements which admit of satisfactory manipulation for quantitative purposes. Moreover, the

gas itself is so light (0·0695 when air = 1) that it tends to diffuse out of all vessels, and is difficult to weigh, so that the direct determination of its atomic weight by the observation of its density (p. 166) is liable to error. Oxygen, on the other hand, forms compounds with most of the elements ; and, in fact, many of the equivalents which have been determined are based upon the analysis of oxygen compounds. This gas has also the advantage of being heavier than air (1·105 when air = 1), so that its density can be determined with less liability to error than hydrogen. For these and other reasons, oxygen is now made the standard of atomic weights ; and in the international list the numbers adopted are relative to that element. It will be understood, therefore, that the weight of the atom of oxygen with reference to hydrogen is a matter of extreme importance. The ratio of oxygen to hydrogen in water obviously furnishes the necessary data ; and the concentration of patience and skill which has been brought to bear upon the determination of that ratio by Morley and others will rank in the future history of Chemistry among the greatest achievements in scientific precision.

The refined experimental methods made use of in fixing this ratio cannot be described

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here. The equivalent 8 for oxygen when
hydrogen $= 1$ (p. 119) must be corrected in the
light of the most precise evidence to 7·94 ;
and so the atomic weight of oxygen on this
scale becomes 15·88.   Or, if 8 is taken as the
equivalent of oxygen, then the atomic weight
of hydrogen becomes 1·008, because 1 : 7·94
$= 1·008 : 8$ (neglecting the last decimals).   The
molecular weight of oxygen is thus 31·76 on
the scale $H = 1$, or 32 on the scale $H = 1·008$;
and the molecular weight of hydrogen is then
2·016.   These results, be it remembered, are
based on experimental determinations ; and
the atomic weights will, therefore, differ
according to the standard adopted, but—
and here the whole mystery should disappear
—the *relative weights* of the atoms towards
each other remain unchanged, and that is all
that we are concerned with in considering
the weight of an atom from the chemical
point of view.   Consider a case.   On the scale
$H = 1$ and $O = 15·88$, the atomic weight of
sulphur is 31·83 ; on the scale $H = 1·008$ and
$O = 16$, it is 32·07.   There is no real discrep-
ancy here—it is simply a question of stand-
ard ; the ratios remain the same :—neglecting
last decimals, 31·83 : 15·88 $= 32·07 : 16$, or
31·83 : 1 $= 32·07 : 1·008$; and so with refer-
ence to the comparison of the weight of the

sulphur atom with the weight of any other atom on the two scales. The two sets of atomic weights now in existence should thus be easily understood; the standard $O = 16$ has been adopted for the reasons already stated. The atomic weights assigned to the elements referred to in the previous chapters have, as far as possible, been taken as whole numbers. It will now be understood that these numbers were used only for the sake of simplicity, and in order to illustrate general principles.

Chemical Arithmetic.—The symbolical language which was introduced in a former chapter (p. 137) is obviously quantitative. The formulæ assigned to atoms and molecules represent so much by weight of the respective elements or compounds, the degree of numerical precision attaching to the symbols being the degree of accuracy with which the relative weights of the atoms have been determined. It will be seen, therefore, that when we know the formula of a compound, or when we know the composition of the products arising from chemical reaction between materials of known composition, we must necessarily bring such symbols into the domain of arithmetical treatment. The construction of a formula from the results of analysis is in itself an

arithmetical problem. For example, water has been said to contain (in round numbers) oxygen and hydrogen in the proportion 8 : 1 —this is the outcome of analysis and synthesis; and, as is the universal custom, the actual numerical results are in the first place stated on the percentage scale; oxygen 88·9, and hydrogen 11·1 per cent., approximately. That gives the ratio 8 : 1. But for the formula we want not the weight ratios only, but the ratios between the numbers of atoms in the molecule. The number of times the atomic weights of oxygen and hydrogen are contained in these percentage numbers will evidently give the required information. Thus $88·9 \div 16 = 5·55$, and $11·1 \div 1 = 11·1$, and so the ratio between *the numbers of atoms* is 5·55 : 11·1; then, since the atom is by hypothesis indivisible, we take the nearest whole numbers, and so make the ratio 1 : 2. The formula is thus found to be H_2O; and if it should happen to be a multiple of this (which in this case it is in the liquid state; p. 172), it makes no difference to the *relative* numbers—the minimum formula only is found by this calculation, and the *molecular formula* of the vapour is settled by the determination of the molecular weight as already explained.

The calculation of a formula from the percentage composition is, therefore, simple enough ; the percentage numbers divided by the atomic weights and the results expressed in the simplest set of whole numbers give the relative numbers of the respective atoms in the molecule ; the actual numbers can only be found when the molecular weight can be determined. Conversely, the formula being known, the percentage composition can be easily calculated. Sugar, for example, is found by analysis to contain carbon, hydrogen, and oxygen in such proportions as to lead to the formula $C_{12}H_{22}O_{11}$ (p. 177). The sum total of the weights of the atoms being in round numbers 342, that weight contains 144 parts of carbon, 22 parts of hydrogen and 176 parts of oxygen, from which fact the weights of carbon, hydrogen and oxygen contained in 100 parts of sugar can obviously be calculated by a very familiar process.

It is unnecessary here to set problems or to work out examples ; we are concerned only with those broad principles which serve to illustrate the enormous power which the atomic theory has placed in the hands of the chemist. An obvious extension of the foregoing principles enables us, for instance, to calculate the theoretical yields of products

resulting from chemical change. Such changes
—chemical reactions—are capable of being
represented in the form of equations showing
the arrangement of the materials before and
after the reaction (pp. 169 and 187). Consider,
by way of illustration, the burning of iron in
oxygen to form scale (p. 23), the decomposition
of water by heated iron to form this same
oxide (p. 81), or the reduction of copper
oxide to copper by means of hydrogen just
referred to (p. 187). The equations are :—

$$3\,Fe + 2\,O_2 = Fe_3O_4 \,;$$
$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2$$
$$CuO + H_2 = H_2O + Cu.$$
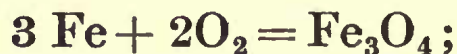
It is obvious that, given the atomic weights,
all these reactions can be dealt with arith-
metically. Using the nearest whole numbers,
3×56 parts of iron yield $3 \times 56 + 16 \times 4$ parts
of magnetic oxide ; 3×56 parts of iron use up
$4 \times (16 + 2)$ parts of water to form the weight
of oxide represented by Fe_3O_4, and liberate 8
parts of hydrogen ; the weight of copper oxide
represented by CuO furnishes the weight of
copper represented by the atomic weight, *i.e.*,
63·6 when $O = 16$, or 63·1 when $H = 1$. From
such data it is, of course, easy to find out how
much magnetic oxide can be obtained from
any given weight of iron, how much hydrogen

a known weight of iron will yield, or how much copper and how much water can be obtained from a certain quantity of copper oxide.

It is needless to enlarge upon this topic, but the practical bearing of theory upon industrial processes finds no better illustration in the whole domain of applied science than in this power of prevision which the chemist is thus enabled to wield. From known weights of materials reacting in a known way and giving rise to known products, it is possible to calculate what the yields should be. Not that *theoretical* yields are often actually realized in practice—there are generally secondary changes, unavoidable losses, and so forth ; but the nearer the theoretical yield the more successful the industry—the transformation of industrial empiricism into scientific procedure is measured quantitatively by the percentage of the theoretical yield. It is only in the most refined laboratory operations that the requirements of theory and the results of experiment coincide.

Volumetric Relationships.—The volumes occupied by known weights of gaseous compounds being known, it is evident that here also arithmetical treatment is possible. Facts and arguments have already made it

clear to the reader that in the gaseous state
the *molecular weights* of all non-dissociable
elements and compounds occupy the same
volumes. This is the obverse side of the
hypothesis of Avogadro (p. 157). In order
to simplify matters, we can, therefore, take
as reference unit some standard element of
which the volume of a given weight is known
with accuracy. In fact, the molecule of
hydrogen in grams, $2 \times 1 \cdot 008 = 2 \cdot 016$ (p. 194),
occupies $22 \cdot 4$ litres at the standard tempera-
ture and pressure of $0°$ and 760 mm. The
gram-molecule of every non-dissociable element
and compound, therefore, under these com-
parable conditions fills a space of $22 \cdot 4$ litres.
The rest is simple arithmetic. A given weight,
say of iron, yields so much by weight of
hydrogen : $2 \cdot 016$ grams of hydrogen at $0°$
and 760 mm. occupy $22 \cdot 4$ litres ; therefore
the volume of hydrogen liberated by the
given weight of iron will be so many litres
under similar conditions. Again, carbon
$(C = 12)$ when heated in oxygen burns, *i.e.*,
undergoes combustion with the formation of
the dioxide, CO_2 (p. 125). The reaction is
$C + O_2 = CO_2$, whence 12 grams of carbon
give $12 + (16 \times 2) = 44$ grams of the dioxide.
That weight occupies the same volume as the
molecule of hydrogen under comparable con-

ditions—it is the gram-molecule of carbon dioxide; so that if 12 grams of carbon give 22·4 litres of the dioxide under the conditions specified, the volume of gas given by any specified weight of carbon can be calculated.

From the conception of equimolecular weights, and therefore of equal numbers of molecules of elements and compounds occupying equal volumes under comparable conditions, it is but a natural step to the conception of solutions containing equal numbers of molecules in equal volumes. Such solutions can, of course, be prepared. The molecular weight, or some known fraction of that weight, in grams of any compound AB dissolved in some standard volume of a liquid, say water, contains a known weight of AB per cubic centimetre. The standard used is the litre (1000 cubic centimetres), and a solution containing the gram molecule AB per litre is called a normal solution. This solution can be diluted with water if necessary, and made up to any required volume so as to be semi-normal ($\frac{1}{2}$ AB per litre), deci-normal ($\frac{1}{10}$ AB per litre), and so forth. The point is that such solutions contain known quantities of AB per cubic centimetre, and can be measured out with great accuracy by suitable apparatus.

Supposing, now, that the compound AB is

capable of reacting with another compound
CD in solution, so as to form new substances
by interchange of components, then we have
a chemical change brought about by what is
termed *double decomposition*. Such change
can be expressed by the usual equation :
AB + CD = AC + BD, and in this form can
be dealt with arithmetically. It will be seen
that we have in this case quantities of two
compounds which may be regarded as chemi-
cally equivalent (p. 121). If, therefore, the
precise point could be detected at which, on
adding the solution of AB, the whole quantity
of CD present was transformed by interaction
with AB into the two new substances, we
should be enabled to determine the weight
of CD in a solution containing an unknown
quantity of that compound. In other words,
if a solution of AB of known value is mixed
continuously with the solution of CD and the
addition arrested at the precise point when the
equivalent weight of AB has been added,
we can calculate the quantity of CD present
in its solution. The weight of AB is known
from the measured volume delivered ; the
weight of CD contained in a measured volume
of its solution is at first unknown, but the
weight equivalent to so many grams or frac-
tions of grams of AB is settled by the weight

of AB added. So many cubic centimetres of the solution of CD required so many cubic centimetres of the solution of AB to hit the point of equivalence—the rest is a matter of arithmetic.

All these conditions can be realized experimentally. There are large numbers of chemical reactions of this type which are so sharp that the exact point when equivalence between the reacting materials has been struck can be indicated by the change of colour of some added substance which is not chemically concerned in the reaction (known as an indicator), or by other means. On this principle—which is necessarily outlined here only in a very broad way—there is founded a largely used and beautifully delicate method of determining with very great precision the actual weights of substances contained in solutions. It is the method appropriately known as *Volumetric Analysis.*

CHAPTER IX

VALENCY—CHEMICAL STRUCTURE—THE
CHEMISTRY OF CARBON—STEREO-
CHEMISTRY

Valency.—In its simplest aspect, chemical combination is, from the point of view now reached, union between elementary atoms. The equivalent being that weight of an element which combines with or replaces one part by weight, *i.e.*, one atom of hydrogen (p. 119), it follows that the number of times the equivalent is contained in the atomic weight of any particular element will represent the capacity of that particular atom for combining with hydrogen. If the element does not form compounds with hydrogen, then the number expresses the combining capacity of the atom for some other atom which is equivalent to the hydrogen atom. The principle is a familiar one—atoms which are equivalent to the same atom (hydrogen) are equivalent to one another. A new property of the chemical atom is thus brought out, viz., its

value as measured by the number of atoms of hydrogen or equivalent atoms with which it can combine. This property is appropriately described as the *valency* of the atom. If the atomic weight contains the equivalent once, *i.e.*, if the equivalent and atomic weight are identical, that atom can combine only with one atom of hydrogen or of chlorine, bromine, etc. The formulæ of the compounds HCl, HBr, etc. (p. 165), express this fact. If the equivalent is contained twice in the atomic weight, then that atom can obviously combine with two atoms of hydrogen, chlorine, etc. ; if it is contained three times in the atomic weight, the combining capacity or valency of the atom is three, and so forth.

In the light of this principle, consider some of the compounds which have already been made use of for the purpose of illustrating other principles. The atomic weight of oxygen (16) contains two equivalents (8) ; the atom of oxygen can therefore combine with two atoms of hydrogen, as in water, H_2O. The atomic weight of nitrogen (taken as 14) contains the equivalent ($4\frac{2}{3}$) three times, so that the nitrogen atom combines with three atoms of hydrogen, as in ammonia, NH_3. Again, the atomic weight of carbon (taken as

12) contains the lowest equivalent (3) four
times; the simplest known compound of
carbon with hydrogen is methane, or marsh
gas, CH_4, the gas which is formed by the
decay of vegetable matter under water, and
which rises in bubbles to the surface when the
mud at the bottom of a stagnant pond is
stirred up.   Moreover, since one atom of car-
bon can combine with or be saturated by four
atoms of hydrogen, and since two atoms of
hydrogen combine with one atom of oxygen,
two atoms of oxygen are equivalent in com-
bining value to four atoms of hydrogen; and
so the oxide of carbon referred to as the product
of the burning of carbon in oxygen (p. 125) is
the dioxide, CO_2.

The broad principle of valency should now
become clear without further illustration.
It will be seen that we have in this doctrine a
means of classifying the atoms irrespective
of their nature, *i.e.*, of the kind of elementary
matter built up of such atoms.   Hydrogen,
chlorine, etc., are univalent elements, oxygen
bivalent, nitrogen tervalent, carbon quadri-
valent, and so forth.   It will be seen, also,
that the valency is not always a fixed number,
but, since an element can have more than one
equivalent, in some cases the atom must
have more than one valency.   Carbon, for

example, is generally quadrivalent, but in some of its compounds it may be bivalent; iron in the oxide FeO and in the iodide, FeI_2 (p. 38) is bivalent, in the oxide of rust, Fe_2O_3, it may be tervalent or quadrivalent. Sulphur is quadrivalent in the dioxide, which is formed when the element burns in air, SO_2 (p. 128); the latter can be made to combine with another atom of oxygen to form a trioxide, SO_3, (p. 128), in which the sulphur atom, being combined with 3 bivalent oxygen atoms, is itself sexavalent. Moreover, sulphur forms a gaseous compound with hydrogen, hydrogen sulphide or sulphuretted hydrogen, in which one atom of sulphur is combined with two atoms of hydrogen, SH_2; the atom is bivalent.

The conception of valency may, perhaps, on these grounds, be regarded as somewhat vague; nevertheless, as will be seen immediately, with all its imperfections it has played an exceedingly important part in the development of modern Chemistry. It corresponds with some underlying reality; whether it is an inherent property of the atom as an individual particle, or the result of the interaction of reciprocal forces exerted between combining atoms, cannot at present be decided. It is an empirical doctrine as it

stands—it is descriptive rather than explanatory; yet it describes some faculty potentially or actually present in the atomic mechanism. It serves as a check upon chemical formulation, and yet it fails to explain why any particular formula is possible. In other words, it enables us to assert that, when combination does take place, certain rules—more or less elastic—are obeyed. But it does not tell us why this, that, or the other atom can combine with certain atoms and not with others; it takes no account of selective idiosyncrasies beyond representing the facts which are the expressions of these idiosyncrasies. The fact that valency is associated with certain physical properties of the atom is sufficient indication that there is an underlying reality.

Consider, for instance, the fact that the same electric current causes the liberation of equivalent weights of chemical elements (p. 121). This may be interpreted as an indication that equivalent weights of the elements are associated with equal quantities of electricity —that chemically equivalent weights are also electrically equivalent. One step further, and we arrive at the conclusion that, if an element of which the equivalent and atomic weights are identical is associated with one

unit of electricity, an atom of which the atomic weight is n times the equivalent must carry n units of electricity. In other words, a hint that valency may be connected with, if not actually expressive of, the electric constitution of the atom is hereby suggested (Helmholtz, 1881).

Again, if the capacity for combination possessed by various atoms is expressed as a geometrical conception, it may be considered that the space required for the grouping of the attached atoms to the central attracting atom will be larger in proportion with the increase of valency of the latter. The "sphere of influence" of a bivalent atom would be double that of a univalent atom, of a quadrivalent atom four times that of a univalent atom and so forth. Here, also, there is correspondence with fact; the packing in space of the atoms which build up a molecule, finds external expression in the regular crystalline form which characterises the majority of definite chemical compounds. There is correspondence between the architecture of the solid crystal, regarded as a structure built up of molecules, and the volume occupied by these molecules regarded as assemblages of atoms, each occupying its own "sphere of influence" (Barlow and

o

Pope, 1906). The conception of the valency of the atom, evolved originally from the study of chemical compounds (Frankland, 1853 ; Kekulé, 1860), has thus been extended into the domain of Crystallography, that branch of science which is concerned with the study of the definite geometrical forms assumed by elements and compounds under appropriate conditions.

Chemical Structure.—The actual grouping of the atoms composing a molecule may at first sight appear to be a problem beyond human ken. Nevertheless the doctrine of valency, in spite of its incompleteness, has enabled chemists to make enormous advances in this direction. The study of chemical composition and decomposition—of the results of dissecting the molecule piecemeal and, when possible, of reconstructing it from its component atoms—renders it possible to form a mental picture of the way in which the atoms are grouped. That mental picture was a blurred and imperfect representation until, at the touch of the conception of valency, definiteness was substituted for vagueness, and the chemist provided with a means of translating his crude imagery into manageable formulæ.

This development is made possible by

the simple device of joining the atoms together —not in an arbitrary way, as has been done in the preceding chapters, but in the order which represents the actual state of their combination. Furthermore, the combination between the atoms is, so to say, visualised by giving each atom its valency, and by imagining that the lines of force which bind the atoms are real lines. These " bonds " are, of course, imaginary; they have no more real existence than the " lines of force " round the poles of a magnet. It is not even necessary in practice to use lines at all; dots will do equally well, and enable the formulæ to be written much more concisely. Begin with an abstract case, and the principle will become clear.

A molecule is composed, say, of AB_2C. The mere juxtaposition of symbols here indicates chemical union, but the formula does not show how the atoms are grouped —whether A is combined with B or with C, or with both; whether B is combined with B or with A or C, and so forth. Supposing now that it was known definitely from the mode of decomposition of the molecule that C was combined with A, and also with both atoms of B, then the formula would more nearly express the facts if it were written

ACB_2. But each of the atoms concerned in building up this molecule has its propei valency, and can therefore be " bonded " with its associates in such a way as to indicate the full structure or mode of grouping thus,

$A=C \diagdown{\Large \begin{matrix} B \\ B \end{matrix}}$ or, more briefly, $A:C:B_2$, in which formulæ it will be seen that A is bivalent, C quadrivalent and B univalent. This is a type of what is known as a *structural* or *constitutional formula*. Such a formula is obviously more expressive of the reality of structure than the *empirical formula* AB_2C, which tells us nothing more than that the molecule contains one atom of A, two of B, and one of C. All the compounds which have been referred to in former chapters can be formulated on this principle. Thus, $H-Cl$; $H-O-H$, $N \equiv H_3$, $C \equiv H_4$, $C = O$, $O = C = O$, $Fe = I_2$, $Fe = S$, etc., stand as structural formulæ for hydrogen chloride, water, ammonia, methane, carbon monoxide, carbon dioxide, ferrous iodide, ferrous sulphide. The valencies of the atoms are evident in such formulæ ; not only the simple valencies of elements in which the atomic and equivalent weights are identical, but also the variable valencies due to multiple equivalence, as in the case of the above oxides of carbon, in which the atom

may be bivalent or quadrivalent, or in sulphuretted hydrogen and the oxides of sulphur (p. 128) :—

$$\text{H–S–H,} \quad \text{O}{=}\text{S}{=}\text{O,} \quad \text{O}{=}\text{S}\Big\langle\begin{array}{c}\text{O}\\\text{O}\end{array}\Big.,$$ in which

sulphur is bivalent, quadrivalent, or sexavalent.

Structural or constitutional formulæ must obviously increase in complexity with increase in the number of atoms composing the molecules. They may be written fully spread out with all the bonds represented by lines, and so expressed as " graphic formulæ," although in practice the chemist soon becomes accustomed to substitute dots for lines, and to pack up the symbols so as to occupy as little space as possible. The significance of the formula is in no way impaired by such condensation. It will be realized that this method of formulation corresponds with something very real, since it expresses the sum total of ascertained fact—it is the pictorial representation of the mode of attachment of the various atoms in a molecule as ascertained by experiment. The chemical structure of a molecule is not a purely mathematical problem in permutations and combinations ; it is something more than this—it is a problem in permutations and combinations controlled

by fixed molecular architectural requirements necessitated by the valencies of the atoms.

The conception of chemical structure is obviously of the same order as the conception of valency upon which it is founded—it is descriptive rather than explanatory. The experimental evidence upon which a structural formula is based is often difficult to obtain, and still more frequently difficult to interpret. The final aim of the investigator is to be able to represent the atomic structure of molecules by such formulæ. The progress which has been made in this direction is synonymous with the progress of modern Chemistry. By every available method of attack is this problem approached—by pulling down and building up by chemical methods, or by comparative physical methods starting from certain measurable physical properties correlated with simple compounds of known structure, and extending the results to molecules of greater and greater complexity. Such imperfection as exists in our structural formulæ is due partly to imperfect information concerning the actual mode of grouping of the atoms, and partly to that empiricism which at present attaches to the conception of valency. In a molecule composed of a few

atoms, the possibilities of grouping are necessarily limited; when, as in the case of many of the highly complex compounds of carbon which build up the tissues of living organisms, we have molecules composed of hundreds of atoms, we have passed into a new order of things—a domain at present beyond the resources of structural formulation.

So, also, with respect to the graphic representation of definite compounds of known structure, there are limitations imposed by our ignorance of the true cause of valency. Thus, when a structural formula has been assigned to a particular compound, and all the maximum valencies of the various atoms have been accounted for, the molecule as a whole may still possess the faculty of combining with other molecules. In other words, molecules, the valencies of the atoms of which are all apparently in chemical language *saturated*, may still behave as *unsaturated*. Such molecular compounds are quite definite, but a new order of combination appears to come into play. Many metallic salts, for instance, combine with definite quantities of water of crystallization, or with definite numbers of molecules of ammonia or other compounds. The oxide of iron of " scale," Fe_3O_4, may be a molecular compound of

FeO and Fe_2O_3. Thus it has been found necessary to extend the main doctrine by recognizing residual affinities, partial valencies, auxiliary valencies, etc. A new field has, in fact, been opened up in this direction; and the completion of the theory of valency cannot be looked for until this field has been more extensively cultivated. The pioneers are at work, and considerable advances have been made of late years.

But the defects of the theory which have been indicated in no way detract from its utility as a means of representing chemical structure as far as its applications can be pushed. The bare recognition of the principle that chemical character and atomic configuration are interdependent marks an epoch in chemical thought. Thus, it has long been known that certain elements are capable of existing in different forms—the so-called *allotropic modifications*. Oxygen, for instance, under the influence of the silent electric discharge assumes a different and more active form known as *ozone*. In this case there is no transformation of matter; ozone is still at basis oxygen. It is known that the change in character is due to a difference in the state of aggregation, the molecule of ozone being triatomic, O_3, whereas oxygen is diatomic,

O_2 (p. 160). This is proved by the vapour density of ozone, or by the conversion of a known quantity of ozone into oxygen by the action of heat. Oxygen being bivalent or quadrivalent, the structural formula of oxygen would be O : O, and of ozone $O \overset{\cdot}{O} O$ or O : O : O. Carbon, again, as an element is the same " stuff " whether transparent and crystalline, as in the diamond, or black and opaque as in graphite and charcoal. Phosphorus, also, may be an exceedingly inflammable wax-like solid with a low melting-point, or a comparatively inert reddish powder : The two forms are interconvertible.

Such cases are possibly explained by differences in the state of atomic aggregation —they may belong to the same category as oxygen and ozone, only the molecular weight of solid carbon or red phosphorus cannot, for the reasons already set forth (p. 172), at present be determined ; and so the actual numbers of atoms contained in the different modifications cannot be definitely fixed. But independently of the question of molecular weight, the conception of structure asserts itself. A difference of molecular aggregation in a sense implies difference of structure ; but it will also be seen that there might be difference of structure due to different configurations of

atoms within the same molecule. Sulphur, for example, exists in several modifications, four solid and crystalline, one a yellow mobile liquid (119° — 160°), one a dark viscous substance (160° — 448·5°), and a vapour above the latter temperature. The vapour exists, as we know (p. 167), in different states of atomic aggregation. The differences between the crystalline forms are probably due to differences of molecular arrangement, *i.e.*, to physical structure; the difference between the solid and the other forms may be due to differences of atomic aggregation, as with oxygen and ozone; while the difference between the liquid and viscous forms may be due either to differences of atomic aggregation or to differences of atomic grouping within the molecule. It is evident that the decision between molecular grouping, atomic aggregation, and differences of intra-molecular structure can only be given when the molecular weights of the solid and liquid forms can be determined.

The Chemistry of Carbon.—While the conception of structure can at present be borne in mind in its possible application to such cases as the above, the triumph of the theory finds full expression in the domain of what is called *Organic Chemistry.* This term is a

survival from a period when the compounds
dealt with under this division were supposed
to be producible only through living agency,
i.e., by organisms belonging to the animal or
vegetable kingdom. With the progress of
science, this meaning of the term " organic "
disappears, since large numbers of these
compounds—identical with the natural pro-
ducts—are now produced by synthetical
methods in our laboratories, and many of them
of technical use are manufactured on a colossal
scale. Organic Chemistry is, in fact, the
chemistry of carbon, since it is this element
which, in combination with a few other
elements, notably hydrogen, oxygen, and
nitrogen, gives rise to the vast multitude of
compounds of every degree of complexity
which constitute the materials which, with
certain mineral or inorganic constituents,
build up all animals and plants. The ques-
tion whether " vitality " may be a function
of the special chemical and physical properties
due to the association of carbon with certain
other elements is of profound interest, but
cannot be discussed here. To the chemist,
organic matter is carbonaceous matter ; mod-
ern science knows of no " vitalism " apart
from carbon compounds.

The division of Chemistry into inorganic

and organic is now only a matter of convenience arising from the enormous mass of material supplied by carbon chemistry. Over 150,000 definite " organic " compounds are known, a small fraction only of this number being the products of " vitality." The remainder are all artificial—synthetical compounds unknown in nature till called into existence by the exercise of the power of chemical science over the inner constitution of molecules, a power made possible mainly by the theory of structure based upon valency. In recording this triumphant success of synthetical chemistry, it must be emphasized that there has as yet been produced in the laboratory no compound possessing in the least degree those characters which pertain to living organic matter. The great and fundamental problem of bridging the gap between living and dead matter still remains unsolved; it may remain unsolved for all time, or it may not. For aught that we know, Nature may be solving this problem daily under our eyes, but her methods have as yet remained unrevealed. Any revelation in this direction that awaits the science of the future must perforce be through Organic Chemistry.

The potency of structural formulation as

a means of giving expression to molecular structure is manifest among carbon compounds in every direction. The applications are so numerous—the field is so vast that only the barest hints can be thrown out in this volume. It will be perceived as a general principle that, with increase in complexity, *i.e.*, with increase in the number of atoms composing the molecule, there must result a continually and rapidly augmenting number of possible formulæ. Are these formulæ real ?—does each different configuration of atoms correspond with some definite chemical compound ?—in brief, how far do such graphic representations express the facts of chemical science ?

The answer to these questions carries with it the vindication of the claim of the theory of structure to run parallel with, if not actually to represent, the underlying physical reality of the atomic configuration of molecules. So close is the correspondence between theory and observation that, given the number of atoms composing a molecule, it is possible to predict the number of compounds that ought to exist, with full confidence that such compounds may actually be obtainable. In hundreds of the simpler cases, the correspondence of theory with fact is complete—

every compound required by theory has been prepared. There, thus emerges the great principle of *isomerism*, which simply indicates that totally different compounds may be built up of the same numbers of atoms of the same elements. It is not only the total number of atoms, but the grouping of the atoms within the molecule that is the determining cause of individuality. A phenomenon which at first appeared at variance with all common sense notions—the fact which staggered the early investigators in this field, viz., that two or more molecules might have precisely the same ultimate composition, and yet be quite distinct forms of matter, has become a commonplace doctrine in modern science in the light of the theory of chemical structure. Moreover, the development of structural chemistry has of late years led to the recognition of the internal mobility of atoms within molecules—of structural configurations so delicately balanced that the atoms constituting the molecule may assume one or another of two quite different configurations according to the conditions to which it is exposed. To this phenomenon, the general term *tautomerism* is applied.

Stereochemistry.—Yet another step in the theory of chemical structure, and we are

face to face with one of the most brilliant of modern achievements in the direction of bringing Chemistry into the category of the deductive sciences. The atoms composing a molecule must obviously form a group in space—the configuration is not that of a congeries of points all lying in one plane, but a system occupying tridimensional space. This conception was first definitely applied to the structural formulation of carbon compounds by Le Bel and van't Hoff in 1874. The four " bonds " of the carbon atom, for example, may be represented by lines radiating symmetrically from the carbon atom as a centre. This is expressed geometrically by supposing that the carbon atom is in the centre of a regular tetrahedron, the points of the angles of which represent the terminations of the bonds to which are attached the other atoms or groups of atoms which build up the molecule. If the carbon atom, regarded from this point of view, is combined with four different atoms or groups of atoms, there then arises as a geometrical necessity the existence of two different space groupings of the same molecule which are non-superposable, and which are related to each other in the same way that an object is related to its reflected image in a mirror—a right and a left-handed

isomerism quite incapable of being represented by any formula which ignores the space configuration of the atoms. This conception in its modern developments may almost be said to complete the theory of isomerism; large numbers of cases in which the differences between compounds of the same ultimate composition cannot be expressed by plane surface structural formulæ are now known to be cases of *stereochemical isomerism*. This newer development of the atomic theory—known as Stereochemistry—is gradually pervading and making its influence felt throughout the whole domain of our science. The fundamental idea of space grouping is not easy to follow at first without the aid of models, but the modern student is being taught to handle these formulæ which, by virtue of their rationality, are bound to dominate more and more all our notions concerning the structure of molecules.

The possibilities of isomerism, regarded from the stereochemical point of view, naturally become more complex with the increase in the number of carbon atoms which comply with the conditions of asymmetry just defined. Here, again, is there close parallelism between deduction from the theory and observed facts —an everlasting testimony to the fertility

of the idea. Thus, the acid of sour milk, lactic acid, contains an asymmetric carbon atom, and exists in two stereochemical forms, as required by theory; tartaric acid contained in the juice of grape and other fruits contains two asymmetric carbon atoms, and exists in three stereo-isomeric forms as required by theory. The group of sugars typified by grape sugar, or glucose, comprised under the formula $C_6H_{12}O_6$, contain four asymmetric carbon atoms, and can exist in sixteen stereo-isomeric forms. Many of these sugars are natural products; and nearly the whole series of sixteen required by theory has been synthesized by Emil Fischer and his colleagues—a veritable triumph of modern carbon chemistry.

One of the chief points of interest arising from space formulation is the correspondence between configuration and a certain physical property, viz., that of *optical activity*, by virtue of which certain compounds possess the power of causing the rotation of polarized light in either a right-handed (dextro) or left-handed (lævo) direction. It is, in fact, by this character alone that the stereo-isomerism is in most cases revealed, since such isomerides, unlike ordinary isomerides, are alike in all other physical and chemical characters. In the light of Stereo-chemistry, optical activity

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is shown to be associated with this intra-molecular asymmetry. Physics, Chemistry, and Biology herein find another common meeting ground, since it is to Physics that we look for the explanation of the mechanism of the connection between asymmetry and optical activity; while the chemical processes which go on in the living organism frequently result in the apparently direct production of optically active carbon compounds—an achievement which some chemists believe to be an essential privilege of " vitalism." But laboratory syntheses also result in optically active compounds; the lactic and tartaric acids, the 6-carbon-atom sugars, and hosts of other compounds have all been synthesized in their stereo-isomeric optically active forms. The main difference is that biochemical synthesis is directive in the sense of leading to the final production of the optically active compound, while laboratory synthesis is at present without such directive power—the two possible configurations are produced simultaneously, and the final product is, therefore, optically inactive by compensation. But such inactive compounds can be afterwards separated or resolved into their stereo-isomerides by temporary combination with other active compounds of vital origin. With the

solution of the fundamental problem of controlling laboratory synthesis so as to suppress the production of the one or the other of the possible intra-molecular configurations, the temporary aid of the optically active vital compound would be dispensed with. There would then disappear another of the barriers which have been erected between living and dead organic matter.

The asymmetry possible for a quadrivalent atom, such as carbon, is obviously conceivable in the case of other atoms. The hint given by carbon chemistry has been taken with all the seriousness which attaches to what the man of science knows to be a great truth. Other quadrivalent elements, such as tin, silicon, and sulphur; quinquevalent elements such as nitrogen and phosphorus, and, quite recently, the atoms of certain metals such as cobalt, chromium, platinum, and rhodium, have been made to form optically active stereo-isomerides. The reader will realize that this new and vast domain which is being opened up by many workers in many lands invests the atom of modern Chemistry with a reality so vivid that the correspondence between mental imagery and observed fact cannot be said to be surpassed in any of the purely deductive sciences.

CHAPTER X

THE PERIODIC CLASSIFICATION OF THE ELEMENTS—CONCLUSION

A SCIENCE which, in its purely materialistic aspects, claims for its subject matter the study of some eighty odd elements, and all the compounds capable of being formed by these elements, would be but a heterogeneous jumble of facts without guidance from general principles. It has only been possible within the compass of this volume to give the reader a glimpse here and there into some of these principles. The treatment has perforce been narrowly materialistic; and yet it must not be concluded that the chemist takes only into consideration the matter of which the universe is composed. The energy associated with this matter—its distribution during chemical change, the development or absorption of heat as concomitants of chemical transformations, the production of electricity, of light, and, generally, the physical manifestations

resulting from this redistribution of energy are as much within the province of modern Chemistry as is the natural history of the elements and their compounds.   An introductory fragment only has been offered in the hope that a stimulus may be given to the desire for fuller and more specialized study.

With reference to matter as such, it will be readily seen that any scheme which enables the whole body of elements to be grouped and classified according to their natural relationships must mark an advance towards the systematization of our knowledge of the highest order of importance.   That natural relationships exist among the members of chemical families, which possess certain characters in common, and which also show regular gradations of properties when considered in series arranged in the order of their atomic weights, has already been illustrated by reference to the halogens (p. 100).   Any other family, non-metals or metals, might have been made to enforce the same lesson.   But such classification is restricted ; a wider and more comprehensive scheme which embraces all the natural groups or families of elements was first suggested by J. A. R. Newlands in 1864, and was elaborated and put upon a scientific basis by Mendeléeff and Lothar Meyer in 1869.   Brief

	Helium	Lithium	Glucinum	Boron	Carbon	Nitrogen	Oxygen	Fluorine
1st Series :	Helium	Lithium	Glucinum	Boron	Carbon	Nitrogen	Oxygen	Fluorine
Atomic weights :	3·99	6·94	9·1	11	12	14·01	16	19
2nd Series :	Neon	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine
Atomic weights :	20·2	23	24·32	27·1	28·3	31·04	32·07	35·46

consideration to this scheme may be given in this concluding chapter.

If the elements are arranged in the order of their atomic weights, a remarkable recurrence will be noticed after a certain number of elements have been passed through. Thus, omitting hydrogen—which stands in a unique position—a series of eight members must be arranged in order to bring out the fact that with the ninth there begins another series, in which the chemical and physical properties of the first series recur with that modification due to gradational transition illustrated in the case of the halogens. The two series are given here for comparison.

Reading these lists in the first place in horizontal sequence, it will be seen that there is continuous increase in atomic weight from right to left. In the next place, it will be noticed that recurrence of characters takes place after the eighth element (fluorine), this recurrence being made evident by reading the

series vertically—each vertical column as here arranged consists of a pair of elements belonging to the same family. Now, if the whole of the chemical elements are arranged on this principle, there results a general scheme which brings out the fact that not only are the properties of the elements connected with their atomic weights, but that there is periodicity in the relationships. The two series given above consist of eight members each ; after these, the periods become longer, but the relationship between the members of the vertical columns is still maintained— the grouping in these columns is into natural families with ascending atomic weights and consequent gradation of characters. The law expressing this periodicity is known as the Periodic Law ; and the general scheme is the Periodic Classification. The Table (A ; next page) gives the arrangement at a glance, the symbols of the elements being used for the sake of compactness. The atomic weights can be supplied from the international list appended to this chapter.

The first point to which attention is directed is naturally the periodic arrangement, which is the basis of the whole scheme. The Roman numerals in the first horizontal column are group numbers labelling the groups below

A.—*Periodic Classification of the Elements.*

O.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
He	Li	Gl	B	C	N	O	F	
Ne	Na	Mg	Al	Si	P	S	Cl	
A	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni
	Cu	Zn	Ga	Ge	As	Se	Br	
Kr	Rb	Sr	Yt	Zr	Cb	Mo	?	Ru Rh Pd
	Ag	Cd	In	Sn	Sb	Te	I	
Xe	Cs	Ba	La (Rare earth metals) Ce, Pr, Nd, Sa, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu		Ta	W	?	? Os Ir Pt
	Au	Hg	Tl	Pb	Bi			
Nt	Ra			Th		U		

them in the vertical columns. The first two (short) periods, consisting of eight members each, are given on p. 232. The third (long) period begins with argon, and ends with bromine; the fourth (long) period begins with krypton, and ends with iodine. It will be noticed that in these cases the elements of the long periods are arranged in two horizontal series, so as to bring the members of the same family into their respective groups (vertical columns). After the fourth group, the systematic uniformity is no longer maintained, because, following lanthanum, there has to be interpolated a whole cohort of elements which are most closely related among themselves. These are the so-called " rare earth " metals; and for the sake of compactness they are simply inserted *en bloc* in the order of their atomic weights. The list of these metals is probably still incomplete; new members may be isolated as the result of further research. The known metals of this group exist as compounds in a complex mixture of minerals known as monazite sand, which is found in various parts of the world, and which is worked up on the large scale for the manufacture of the earthy mantles used as incandescent gas burners. These mantles are composed mainly of the oxides of thorium and

cerium, supported by a suitable framework.
After these elements, the horizontal series
become fragmentary—they are suggestive of
incomplete periods.

Considering the scheme, in the next place,
with reference to the natural families or
groups in the vertical columns, it will be
seen that the relationships are more faithfully
expressed by a further division into two sub-
groups. This simply indicates that, while
the members of the group as a whole are
closely related chemically, there is a still
closer inner relationship between the members
of the sub-group. These points will be made
clear by a few examples. Thus, in Group I.
will be found the very natural family of metals,
beginning with lithium and ending with
cæsium, known as the alkali metals. Their
oxides form strongly basic, alkaline solutions
(p. 108); and they all form similar types of
compounds. The sub-group—copper, silver
and gold—is related to the alkali metals by
virtue of certain types of compounds which
the metals named are capable of forming;
but the relationship, although confessedly
not very close, is more intimate between the
three metals themselves—they resemble each
other more closely in their general characters
than they do the metals of the alkalis. In

Group II., again, will be found the metals of the "alkaline earths" (calcium, barium, etc.), the oxides of which are alkaline earthy substances typified by lime (p. 102). The metals of the sub-group (glucinum, magnesium, etc.) are naturally related to these, but still more closely related to each other. The halogens (p. 100), as will be seen, fall into Group VII., and are (somewhat remotely) related to manganese.

The general nature of the scheme should be made evident by these examples. It will be seen that, on the whole, chemical dissimilarity characterizes the members of the horizontal series until the period recurs. It would appear as though something added to the mass of the atom caused it to differ *qualitatively* in its chemical characters from its left-hand neighbour until a certain number of additions had been made, when the difference becomes *quantitative* instead of purely qualitative. And yet this principle is not generally complied with. The triplets of Group VIII., for example, are separated out because, among other reasons, they show close resemblance of character among themselves. Still more closely related among themselves are the metals of the "rare earths," the separation of which has necessitated

the most laborious work carried on for very many years. In these cases, there is no abrupt change of character in passing from element to element along the horizontal series. Other discrepancies occur—notably with the elements argon (39.88) and potassium (39.1), which are out of place if the strict order of atomic weights is followed. Iodine (126.92) and tellurium (127.5), have likewise to be taken out of order to bring them into the groups to which they naturally belong. It may be that such discrepancies indicate that the atomic weights need further revision.

Passing over these and certain minor discrepancies as problems yet awaiting solution, the significance of the scheme as a comprehensive whole must be fully realized in order that its systematizing influence upon our science may be adequately appreciated. That it corresponds with some underlying reality is made manifest by the coincidence of periodicity in several distinct sets of characters. The horizontal series, for instance, classified originally simply in the order of the atomic weights, will be found to correspond also with a classification according to valency— due allowance being made for the variability of this property (p. 206). Measuring the valency of the atom by the maximum number of

hydrogen atoms with which it combines if it forms hydrogen compounds, or with halogens if it forms no hydrogen compounds, the valencies of the atoms of the first series may be indicated by attaching small Roman numerals to the symbols :—

He° ; Li^i ; Gl^{ii} ; B^{iii} ; C^{iv} ; N^{iii} ; O^{ii} ; F^i.
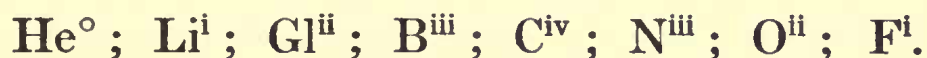
The periodicity here shown is observed also in a precisely similar way in the next series. If the valency is measured by the number of oxygen atoms in the acid and basic oxides in any series which comprises such a set of oxygen compounds, a regular increase is observed :—

2nd Series :—Ne° ; $Na_2^i O^{ii}$; $Mg^{ii}O^{ii}$; $Al_2^{iii}O_3^{ii}$; $Si^{iv}O_2^{ii}$; $P_2^v O_5^{ii}$; $S^{vi}O_3^{ii}$; $Cl_2^{vii}O_7^{ii}$.
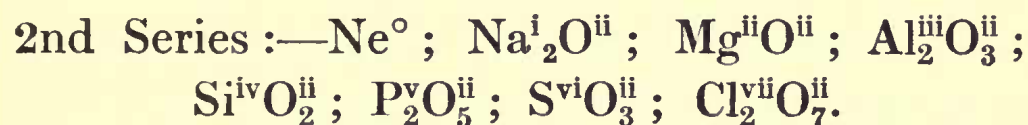
The scheme thus emphasizes the association of chemical character with valency—distinctness marking the transition from member to member along the horizontal series and similarity among the natural groups in the vertical columns. In general terms, the Roman numerals heading the eight columns may be regarded as indexes of valency—not, of course, in too rigid a sense, but as indicating maximum valency. The zero sign over the first column is to be taken literally as meaning no valency. The elements from helium downwards form

no compounds with other elements; they are all chemically inert monatomic gases (p. 170) contained in minute quantities in atmospheric air (p. 46). Their separation has necessarily been effected by physical methods, since, chemically speaking, they are dead matter. Helium, it may be mentioned incidentally, is present in the atmosphere of the sun, and has been found in small quantities in some terrestrial minerals and also dissolved in certain mineral waters. The history of this element is intimately connected with the subject of radioactivity.

The key-note—periodicity—having been struck, the characters of the elements generally will be found to respond. Notice how each period begins with an inert element, and then passes through a series, one extreme of which is an intensely electro-positive base-forming metal, and the other extreme an intensely electro-negative acid-forming non-metal (halogen), the extremes being connected by intermediate elements of decreasingly electro-positive and increasingly electro-negative characters.

Another physical property of the elements, viz., their specific gravity, can also be shown to be conformable with the periodic classification. This conformability is most

strikingly revealed by taking, instead of the specific gravity, the number obtained by dividing the atomic weight by the specific gravity—the so-called "atomic volume," which may be regarded as the volume occupied by the atom of the solid or liquid element. The reader must be careful to distinguish between this "atomic volume" of solid and liquid elements and the volumes occupied by the atomic weights of the elements in the gaseous state (p. 166), in which state only does the hypothesis of Avogadro (p. 153) apply. If the numbers representing the atomic weights (arranged in ascending order) are taken as abscissæ and the numbers representing the atomic volumes as ordinates, the points of intersection, when joined up in the usual way familiar in co-ordinate geometry, give a curve which reveals the periodicity at a glance. The curve thus constructed has a wave-like form ; and the chemically related elements of the natural families occupy corresponding positions on the curve. Thus, the strongly electro-positive alkali metals of Group I. are at the wave summits, the electro-negative halogens of Group VII. at corresponding positions on the ascending slopes, the alkaline earthy metals of Group II. on the descending slopes, and the high melting-point metals of

lower chemical activity belonging chiefly to Group VIII. in the hollows between the waves.

Further details arising from the periodic classification, the critical discussion of its imperfections, and the various suggested amendments must be sought for in the standard works. The value of the scheme—apart from philosophical considerations—is due not only to its systematizing influence, but quite as much to its suggestiveness. It not only consolidates existing knowledge, but it has indicated and still points to gaps in the series which may at some future time be filled. In other words, where the small increment in the numbers representing successive atomic weights suddenly becomes large, a hint is given that one or more elements yet remain to be discovered, or that some of the elements do not occur on this earth. Moreover, since all the properties of the elements and their compounds are gradational in the ascending series of natural groups or families, and since these families all fall into the general scheme, it is possible to predict within narrow limits the properties of missing elements. Two examples of such gaps are inserted in the form of queries in the tabular scheme in Group VII., where there is an

indication of an element having an atomic weight intermediate between molybdenum (96) and ruthenium (101·7) and belonging to the sub-group containing manganese ; and of another element belonging to the same sub-group between tungsten (184) and osmium (190·9).   Hydrogen, which, as already stated, stands at present alone, might be regarded as the only known representative of a series, the members of which, both of higher and (possibly) of lower atomic weight, are missing.

A scheme which harmonizes so many distinct sets of properties might legitimately be used deductively.   The prediction of the properties of missing elements and their compounds illustrates such use ; and the triumph of the scheme dates from the period when certain of the gaps were filled in by newly-discovered elements, the properties of which —as foretold by Mendeléeff—were found to correspond closely with the prediction.   Thus, gallium (Lecoq de Boisbaudran, 1875), scandium (Nilson, 1879), and germanium (Winkler, 1886) all found appropriate niches awaiting them on their discovery.   So also, used deductively, the classification has led both to the revision of atomic weights and to the resortment of elements, *i.e.*, to the transference

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of elements from positions where there was no gap to be filled to positions where they were wanted. This is tantamount to determining the group to which a doubtful element belongs, and so to the determination of its natural relationships and its valency. The scheme thus becomes available as another method of control for deciding in doubtful cases the relationship between the equivalent and the atomic weight (p. 173).

In its philosophical aspects, the periodic classification is naturally suggestive of evolution. Clearly, the elements have not been launched haphazard into existence as independent entities: the contemplation of their various relationships and inter-relationships causes to arise spontaneously the question whether the known forms of elemental matter may not be genetically related—whether the regularities arising from the successive additions to the mass of the atom may not be interpreted in terms of the development of the elements from some primordial " stuff." It may be so—it would only be in harmony with the whole scheme of Nature that such should be the case. The consideration of the various attempts which have been made to prove elemental genesis would, however, take us too far into the region of speculation. The

" Periodic Law " as it stands is, in strict philosophical terms, but an empirical summary —its interpretation has yet to be found.   Is it too great a stretch of prophecy to suggest that the ultimate coalescence of Physics and Chemistry will be brought about through the interpretation of the principle of periodicity ? The actual evidence in support of genetic relationship is at present scanty ;   but it is slowly and surely accumulating in the field of radioactivity.   Here, again, the scheme, as far as it goes, harmonizes with the latest discoveries.   The three elements of highest atomic weight—radium, thorium and uranium, with possibly " radium emanation " or niton— fall naturally into in the last series.   That series may be incomplete—there are gaps which may or may not be filled up by future discovery ;   but it is in this series that the atoms appear to have reached the limit of internal stability.   It is these elements which are undergoing that process of spontaneous decay or disintegration with the liberation of the enormous store of energy which manifests itself in the phenomena of radioactivity.   The final material product of this atomic disinteg- ration which has thus far been definitely identified is the inert gas helium.   It is in this sense, as already stated (p. 90), that transmu-

tation, as distinguished from transformation, receives recognition in modern Chemistry.

CONCLUSION.—The reader who has followed the development of the subject up to this stage will now realize that he has been brought to the threshold of a great edifice crowded with departmental chambers. The various compartments are not watertight divisions—there is free intercommunication by means of cross passages more or less broad and numerous, according to the particular label on the door of the chamber. In this small volume it has not been possible to do more than to point to some of these labels in the hope that the reader may be tempted to explore in greater detail the contents of the various chambers. The inscriptions on a few of these unopened doors are worthy of being noted.

The redistribution of energy which accompanies chemical change is dealt with in works on *Thermochemistry*. When heat is developed as the result of chemical combination, such as when sulphur and iron combine (p. 39), or when carbon burns in oxygen to carbon dioxide (p. 125), and, generally, in all kinds of burning or combustion, the products of such combina-

tion are said to be *exothermic*. Combustion is in fact energetic oxidation. The development of heat in such cases means that the products of combustion contain less energy than the materials which combine—that the system has run down in energy to the extent represented by the heat evolved. On the other hand there are compounds that can only be formed from their elements when energy is supplied from without, because the products contain more energy than their components. These are known as *endothermic* compounds. And thus we enlarge our conception of chemical change by associating the material transformation with the accompanying redistribution of energy. Moreover, the heat evolved or absorbed is as fixed and definite in quantity for each particular chemical change as is the weight of the matter concerned. The change $2H_2 + O_2 = 2H_2O$ to the chemist means the development of 136,800 calories (p. 173) quite as explicitly as it does that four parts by weight of hydrogen and 32 parts of oxygen give 36 parts of water. Thus we come once again into the presence of the chemical atom, now as a definite store of available energy as well as a material particle possessing definite weight.

As the result of the study of chemical change

from the above point of view a quantitative measure of chemical activity has been provided. The " heat of formation " of compounds becomes a measure of the activities of the atoms of the combining elements. It must be noted however that the heat evolved represents but a small fraction of the total internal energy of the atoms. In no ordinary chemical change can it be said that there is tapped more than a definitely limited quantity of this vast store—the greater part of the energy locked up in the chemical atom is still unavailable. The practical solution of the problem of liberating this store of energy—if it is ever solved—would mark the dawn of a new era for the human race.

Then again with respect to the conditions which determine chemical change there is a great field which we have left untrodden. Some of the apparently simplest cases of direct combination reveal their inner complexity through the fact that water vapour —if only a minute trace—is essential for the reaction. Thus $2H_2 + O_2 = 2H_2O$; $H_2 + Cl_2 = 2HCl$; and even $NH_3 + HCl \rightleftharpoons NH_4Cl$ (p. 169) represent chemical changes which do not take place when the gases are absolutely dry. Other chemical changes which at first sight would appear to be quite simple, such, *e.g.*,

as $SO_2 + O = SO_3$ (p. 207), take place only in the presence of heated finely divided platinum or other metals which remain unchanged at the end of the reaction. Metals and other substances which exert this mysterious influence are said to act by *contact* or *catalytically*. It may be that the presence of a catalyst of some kind is a necessary condition of all chemical change.

Among other unconsidered conditions of chemical change is the influence of the active masses of the reacting materials upon the velocity of the reaction (p. 73), upon the direction in which the change takes place in a *reversible reaction* such as $3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$ (pp. 187 and 198), and in determining the actual quantities of the products present when the system reaches equilibrium under various conditions, *i.e.*, when the reversible reaction becomes balanced owing to the velocities of the change in each direction being equal. The contents of the chambers labelled Chemical Statics and Dynamics are well worthy of detailed exploration, for here the reader will find that modern Chemistry has been brought within the reach of mathematical treatment.

1912.—*International Atomic Weights.*

		O = 16.			O = 16.
Aluminium	Al	27·1	Neodymium	Nd	144·3
Antimony	Sb	120·2	Neon	Ne	20·2
Argon	A	39·88	Nickel	Ni	58·68
Arsenic	As	74·96	Niton	Nt	222·4
Barium	Ba	137·37	(radium emanation)		
Bismuth	Bi	208·0	Nitrogen	N	14·01
Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·00	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·6
Chlorine	Cl	35·46	Radium	Ra	225·95
Chromium	Cr	52·0	Rhodium	Rh	102·9
Cobalt	Co	58·97	Rubidium	Rb	85·45
Columbium	Cb	93·5	Ruthenium	Ru	101·7
Copper	Cu	63·57	Samarium	Sa	150·4
Dysprosium	Dy	162·5	Scandium	Sc	44·1
Erbium	Er	167·7	Selenium	Se	79·2
Europium	Eu	152·0	Silicon	Si	28·3
Fluorine	F	19·0	Silver	Ag	107·88
Gadolinium	Gd	157·3	Sodium	Na	23·00
Gallium	Ga	69·9	Strontium	Sr	87·63
Germanium	Ge	72·5	Sulphur	S	32·07
Glucinum	Gl	9·1	Tantalum	Ta	181·5
Gold	Au	197·2	Tellurium	Te	127·5
Helium	He	3·99	Terbium	Tb	159·2
Hydrogen	H	1·008	Thallium	Tl	204·0
Indium	In	114·8	Thorium	Th	232·4
Iodine	I	126·92	Thulium	Tm	168·5
Iridium	Ir	193·1	Tin	Sn	119·0
Iron	Fe	55·84	Titanium	Ti	48·1
Krypton	Kr	82·92	Tungsten	W	184·0
Lanthanum	La	139·0	Uranium	U	238·5
Lead	Pb	207·10	Vanadium	V	51·0
Lithium	Li	6·94	Xenon	Xe	130·2
Lutecium	Lu	174·0	Ytterbium	Yb	172·0
Magnesium	Mg	24·32	(Neoytterbium)		
Manganese	Mn	54·93	Yttrium	Yt	89·0
Mercury	Hg	200·6	Zinc	Zn	65·37
Molybdenum	Mo	96·0	Zirconium	Zr	90·6

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    Good systematic introductory works.

Modern Organic Chemistry : by C. A. Keane. The Walter Scott Publishing Co. A good elementary exposition of the later developments of this branch.

Organic Chemistry for Advanced Students : by **J. B. Cohen.** Edward Arnold. A more elaborate historical treatment of the subject.

Modern Research in Organic Chemistry : by F. G. Pope. Methuen & Co. A concise account of the newer lines of research.

APPLIED CHEMISTRY

Chemistry in Daily Life : by Lassar-Cohn, translated by Pattison Muir. Grevel & Co.

The Romance of Modern Chemistry : by **J. C. Philip.** Seeley & Co.

The Chemistry of Commerce : by **R. Kennedy Duncan.** Harper & Bros.

Chemical Research and National Welfare : by Emil Fischer. Society for Promoting Christian Knowledge.
Four popular works giving an account of the part played by Chemistry in the arts and manufactures and in human welfare generally.

NOTE :—No attempt has been made to include in this list more than a few selected types of the multitudinous elementary and advanced text-books written for students. The great standard works of reference familiar to all workers in Chemistry would naturally be beyond the scope of the ordinary reader who is only desirous of making himself acquainted with the existing state of the science.

INDEX

253